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ENGINEERING AND COST STUDY OF AIR POLLUTION CONTROL FOR THE PETROCHEMICAL INDUSTRY - VOLUME 3

ETHYLENE DICHLORIDE MANUFACTURE BY OXYCHLORINATION

AIR PRODUCTS AND CHEMICALS, INCORPORATED

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

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16. ABSTRACT

This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by twelve distinctly different processes has been selected for this type of in-depth study. Ten volumes, entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006a through j) have been prepared.

A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published separately in a series of four volumes entitled Survey Reports on Atmospheric Emissions from the Petrochemical Industry (EPA-450/3-73-005a, b, c, and d).

This volume covers the manufacture of ethylene dichloride by oxychlorination. Included is a process and industry description, an engineering description of available emission control systems, the cost of these systems, and the financial impact of emission control on the industry. Also presented are suggested air episode procedures and plant inspection procedures.

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PETROCHEMICAL AIR POLLUTION STUDY

INTRODUCTION TO SERIES

This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by 12 distinctly different processes has been selected for this type of in-depth study. These processes are considered to be ones which might warrant standards as a result of their impact on air quality. Ten volumes, entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006a through j) have been prepared.

A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published separately in a series of four volumes entitled Survey Reports on Atmospheric Emissions from the Petrochemical Industry (EPA-450/3-73-005a, b, c and d).

The ten volumes of this series report on carbon black, acrylonitrile, ethylene dichloride, phthalic anhydride (two processes in a single volume), formaldehyde (two processes in two volumes), ethylene oxide (two processes in a single volume) high density polyethylene, polyvinyl chloride and vinyl chloride monomer.

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The study reported in this volume, by its nature, relied on the fullest cooperation of the companies engaged in the production of ethylene dichloride. Had their inputs been withheld, or valueless, the study would not have been possible or at least not as extensive as here reported. Hence, Air Products wishes to acknowledge this cooperation by listing the contributing companies.

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American Chemical Corporation*
B. F. Goodrich Chemical Company
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Diamond Shamrock Chemical Company
Dow Chemical Company
Ethyl Corporation
PPG Industries
Shell Chemical Company
Vulcan Materials Company

*Subsidiary of Stauffer Chemical Company

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SUMMARY

The ethylene dichloride (EDC) industry has been studied to determine the extent of air pollution resulting from the operations of the various plants and processes of the industry. The purpose of the work was to provide the Environmental Protection Agency with a portion of the basic data required in order to reach a decision on the need to promulgate air emission standards for the industry.

It was concluded that because of raw material cost advantages, the advent of the steam cracking process for the production of ethylene has virtually eliminated acetylene as a raw material in the production of EDC. It was further concluded that of the two ethylene based processes (namely oxychlorination and direct chlorination of ethylene) the oxychlorination process is the more significant polluter in terms of both total emissions and degree of difficulty in reducing the emissions. However, in terms of industry growth they are about equally significant because the chief current use for EDC is to produce vinyl chloride monomer (VCM), with anhydrous hydrogen chloride (HCl) being produced as a by-product. HCl is an essential feed to the oxychlorination process and the quantity produced in VCM manufacture is sufficient to produce 50 percent of the EDC feed to the VCM unit. Hence, unless another source of HCl is available or if the EDC is going to other uses, a "balanced" plant results, with 50 percent of its EDC capacity from each of the two ethylene based processes. Obviously, the current national concern over the carcinogenicity of VCM could greatly influence growth of the EDC industry. In the meantime, however, this report is devoted to the study of the oxychlorination process, while the less significantly polluting direct chlorination process is the subject of one section of report number EPA-450/3-73-005b of April, 1974, entitled "Survey Reports on Atmospheric Emissions from the Petrochemical Industry - Volume II".

In general terms, the air emissions from the process fall into the categories of ethylene, non-methane hydrocarbons (mostly chlorinated), carbon monoxide and hydrogen chloride. In addition, small quantities of chlorine are sometimes emitted. As practiced today, virtually no oxides of nitrogen have their origin in the process and all raw materials are essentially sulfur-free thus no oxides of sulfur are produced. The average emission factor for the process is about 0.035 lbs./lb. of EDC produced, over half of which is due to chlorinated hydrocarbons with about one sixth due each to ethylene and carbon monoxide. This amounted to about 120 million lbs. per year of total atmospheric emissions in 1973. If industry growth continues as forecast at that time, and if all new plants are built as currently most typical, then, by 1985 the emissions will be about 300 million lbs. per year.

Most of the plants surveyed have some form of final product recovery/pollution control device on the main process stream before it is released to the atmosphere. Not all of the EDC producers include product fractionation in their reported process but of those that do, only half (two plants) include vent condensers for chlorinated hydrocarbon emission control. However, the average emissions from this source are only about one-seventh of the estimated total. About two percent of the emissions result from the widespread practice of using fixed roof tanks with atmospheric vents for pure EDC storage. It has been concluded that there is no demonstrated technique for making significant reductions in the air emissions from the process, although distillation vent condensers and either floating roof storage tanks or storage vent condensers would result in reduced

SUMMARY (continued)

emissions. Installation of these devices would not lead to any significant financial hardship because the recovered EDC would pay part, if not all, of the cost of the emission control.

The study addressed itself to the task of finding a "feasible" though not "demonstrated" emission control technique for the bulk of the emissions, i.e., the main process vent. It was concluded that some form of incineration could be practiced on this stream and if backed up with scrubbers, emissions would be about six million pounds per year in 1985 (an emission factor of 0.0008 lbs./lb. of EDC) with 90 percent of that total being due to existing plants and 30 percent of the total being due to storage losses from those same existing plants. Four forms of incineration were studied. Two of these, namely a direct fired boiler or a thermal incineratior followed by a waste heat boiler result in energy recovery, while the other two, namely incineration or flaring are both wasteful of energy. Furthermore, flaring results in an increase in hydrochloric acid and chlorine emissions while all four result in an increase in emissions of nitrogen oxides (about one million pounds per year or one-sixth of the total). The report concluded that the most feasible method of emission control on existing plants is to install a thermal incinerator and caustic scrubber on existing main process vents, and a condenser and plume burner on existing distillation vents (this assumes that no use can be made of the steam generating potential of these plants). The report further concluded that the most feasible method of emission control on future plants is to install a condenser on the distillation vent stream and then combine it with the main process vent stream for incineration, waste heat recovery and scrubbing. Floating roof tanks are considered for future pure EDC storage.

It must be emphasized that most of the above control techniques have not been demonstrated commercially. The main problem with incineration of chlorinated effluents is that hydrogen chloride is produced. It is corrosive to metals at high temperatures (above about 600° F) or will form hydrochloric acid if allowed to condense with the combustion water vapor that is present. Hence, a difficult temperature control problem exists. A further problem with incineration of oxychlorination off-gas is its low heating value, requiring substantial quantities of supplemental fuel. However, incinerators for the disposal of both gaseous and liquid chlorinated wastes have been demonstrated in other applications and heat recovery has been deomonstrated on some of these as described in the body of the report. Hence, it can be concluded that it is probably feasible for oxychlorination plants

The capital investment (1973 dollars) required for the most feasible combustion devices, as estimated in the report are about $250,000 per thermal incinerator (two may be deemed essential for reliability) and $35,000 for a plume burner on existing distillation vents. A waste heat boiler will add about $375,000 (and again, two may be required) and the caustic scrubbing system will add either $400,000 or $500,000 depending upon whether or not waste heat recovery is employed. If not, a quench will be required, thus increasing the volumetric throughput of the scrubber. The operating cost of a retrofit incinerator and scrubber will exceed $500,000 per year even if a spare unit is not installed. The addition of a heat recovery unit (either retrofit or on a new plant) will reduce the annual cost by about $100,000. The recommended distillation vent condensers and plume burner (retrofit) will add about $50,000 to the plant's annual income. These estimates all apply to the assume. 700 MM lbs. per year capacity of a "Model Oxychlorination Plant".

SUMMARY (continued)

These are significant costs to the industry with reductions in net profit after taxes to about 75 percent of the case without a vent gas combustion device. This is equivalent to a reduction in return on total investment from nearly 14 percent to nine percent, with the latter figure being based on about 15 percent additional capital. On the other hand, a two percent price increase would restore the net profit and most of the return on investment.

The capital expenditure (1973 dollars) required to effect the reduction in emissions cited above will be about $5,000,000 to retrofit the existing plants with a single incinerator or about $6,500,000 if spares are installed. By 1985, the industry will have invested an additional $9,000,000 in new emission controls, as outlined above, with single incinerators and waste heat boilers or about $14,000,000 if spares are installed. Potentially, the industry total ranges between $14,000,000 and about $21,000,000.

The report cites two concepts for research that could lead to reduced emissions from the oxychlorination process. The first concept involves the use of oxygen rather than air feed to the reactor (this practice is followed in one of the existing process plants) but employs an off-gas recycle to minimize wastes going to the atmosphere. The second concept is also employed in one embodiment of the industry, that is the use of chlorine as part of the oxychlorination process feed. There is undoubtedly research being conducted in both of these areas by today's producers of EDC. An additional area of potentially valuable research that is more general in nature is the design of a chlorinated hydrocarbon incinerator/waste heat recovery system.

I. Introduction

Ethylene dichloride (EDC) is a colorless, oily liquid which is primarily used to produced vinyl chloride monomer.[1] It is also employed in chlorinated solvent manufacture, ethyleneamines production and as a lead scavenger in antiknock fluids.[2]

In the U.S., ethylene dichloride is almost exclusively produced by either direct chlorination or oxychlorination of ethylene. Because of lower feedstock costs, these processes have almost completely replaced the older acetylene plus HCl method. Presently, about 45 percent of the total EDC production is by the oxychlorination route.

Atmospheric pollutants from the direct chlorination process are less than one-fifth of those emitted by the air oxidation method. Atmospheric emissions from oxychloration consist of carbon oxides, light hydrocarbons, chlorinated compounds, nitrogen and water vapor.

Virtually all vinyl chloride manufacturers also produce EDC. Most of these plants employ both direct chlorination and oxychlorination facilities. In producing vinyl chloride from ethylene dichloride, HCl is liberated. The HCl plus ethylene is used as feed in the oxychlorination unit. Normally, EDC production is balanced between the two chlorination processes so that no net HCl is produced or consumed.

A process description, industry survey of emission sources, effluent characteristics, control practices and equipment in addition to plant economics for EDC production by oxychlorination are presented in this report. Data for the direct chlorination process were provided in a separate report entitled "Survey Reports on Atmospheric Emissions from the Petrochemical Industry - Volume II" and numbered EPA-450/3-73-005-b.

II. Process Description and Typical Material Balance

Several U.S. companies license oxychlorination processes for producing ethylene dichloride and several others employ their own technology.

The basic chemical equation for the various oxychlorination processes is as follows:

$$2\ CH_2{=}CH_2 + O_2 + 4\ HCl \longrightarrow 2\ CH_2Cl{-}CH_2Cl + 2\ H_2O$$

Approximately stoichiometric proportions of ethylene, anhydrous hydrogen chloride and air (except one plant which uses pure oxygen) are fed to a catalytic reactor which operates at low pressure (20 - 75 PSIG) and 400 to 600° F. Once through flow is used since conversion of ethylene is virtually complete. Because of the high exothermic heat of reaction (>1000 BTU/lb. of EDC produced), efficient heat removal in the reactor is important for adequate temperature control. For this reason, some processes utilize fluid bed reactors [3] with internal cooling coils while at least one producer employs fixed bed multi-tube reactors which resemble heat exchangers.[4] In this design, catalyst is contained inside the tubes and a coolant flows through the shell. In both fluid bed and tubular reactors, most of the heat removed is recovered as steam.

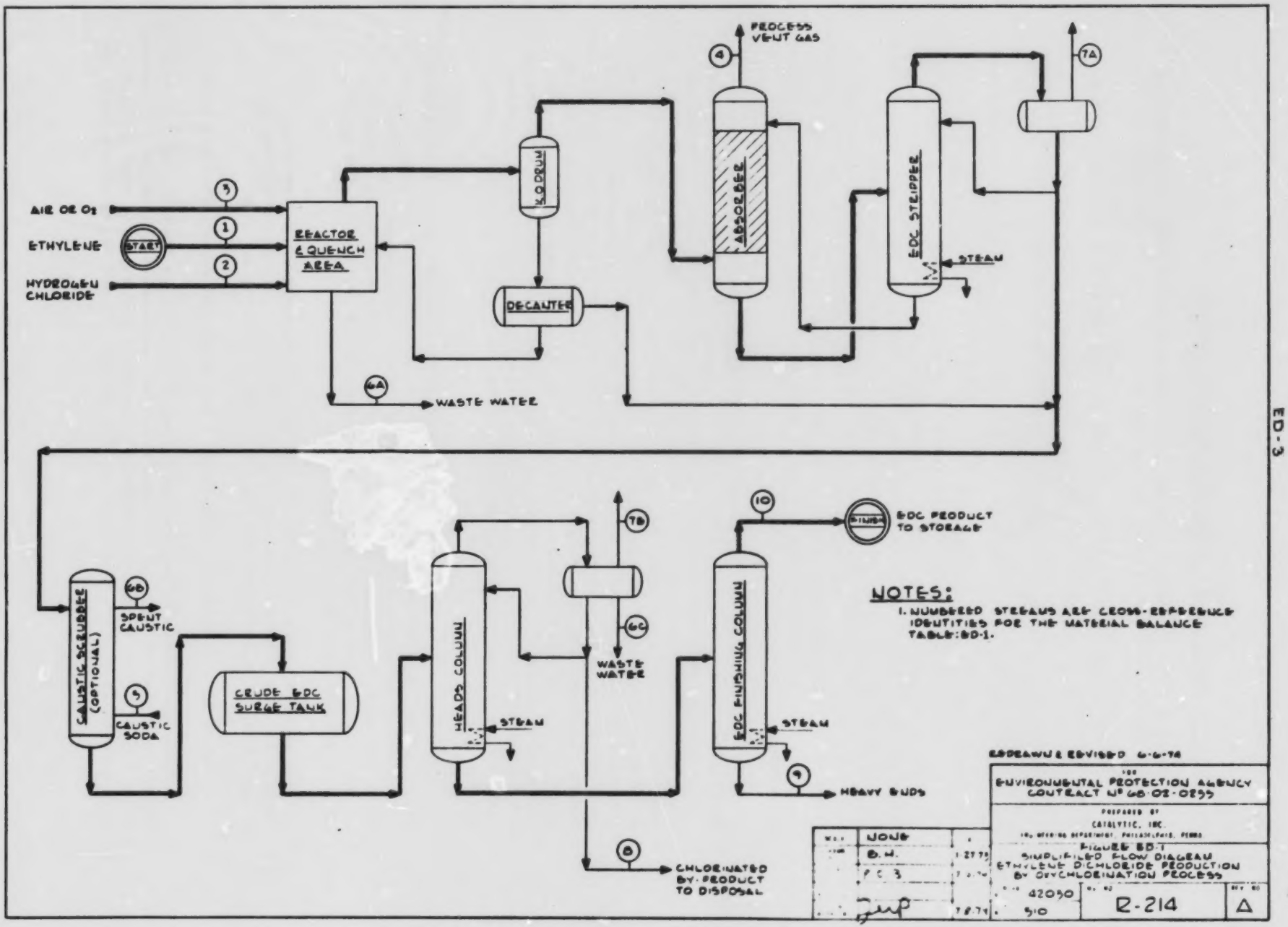
The reactor effluent is normally cooled by either direct water quench or indirect heat exchange. After trim cooling with water and brine condensers, the partially condensed effluent is sent to a phase separator. Non-condensible gases consisting mainly of nitrogen are vented to the atmosphere. Before venting, usually these gases are contacted with either water or aromatic solvent for removal of HCl and recovery of ethylene dichloride. One process incorporates chlorine addition downstream of the main oxychlorination reactor in order to convert unreacted ethylene to EDC. In addition to reducing ethylene loss in the vent gas, the direct chlorination step reduces the amount of air required for oxychlorination. Therefore, the total volume of vent gas and hydrocarbon emissions are reduced in volume. The total volume of vent gas is even smaller for the one unit incorporating tonnage oxygen. For a detailed description of the atmospheric emissions from the various processes, see Section III.

The organic liquid product from the reactor effluent phase separator is either contacted with aqueous caustic soda or sent directly to product distillation for removal of water and chlorinated hydrocarbon impurities which are sent to off-site disposal. In some plants final product distillation is not provided since the crude ethylene dichloride purity (96 - 98 percent EDC) is adequate for many applications.

An aqueous phase collected in the effluent separator is discharged to waste. In some plants dissolved organic materials are removed and recovered in stripping columns before the aqueous stream is rejected.

Figure ED-1 presents a flow diagram for a typical oxychlorination plant.

Table ED-1 shows a "typical" material balance for a "model plant" producing 700 MM lbs./year of EDC. This production rate represents an estimate of average plant capacity for future new units. Table ED-1A presents the same balance with quantities expressed as tons per ton of EDC. These balances are based on



NOTES:

1. NUMBERED STREAMS ARE CROSS-REFERENCE IDENTITIES FOR THE MATERIAL BALANCE TABLE: ED-1.

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	JONES	
	B.W.	1 27 79
	P C 3	7 2 79
		7 8 79

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FIGURE ED-1
SIMPLIFIED FLOW DIAGRAM
ETHYLENE DICHLORIDE PRODUCTION
BY OXYCHLORINATION PROCESS

42050	510	E-214	Δ

ED-3

TABLE ED-1
TYPICAL MATERIAL BALANCE FOR
PRODUCING 700 MM LBS./YR. ETHYLENE DICHLORIDE
BY OXYCHLORINATION PROCESS

	1	2	3	4	5	6	7	8	9	10
Component	Ethylene	Hydrogen Chloride	Air	Process Vent Gas	Dilute Caustic	Combined Waste Water	Distillation Vent Gas	Chlorinated By-Product	Heavy Ends	EDC Product
Carbon Dioxide				2,110						
Carbon Monoxide				583						
Nitrogen			69,672	69,612			60			
Oxygen			21,158	3,912						
Methane		172		172						
Ethylene	27,222			420			9			
Ethane	28	172		575			18			
Ethylene Dichloride				600			386	317	215	85,784
Ethyl Chloride				510			172	26		
Vinyl Chloride							18			
Dichloroethylene							214	34		
Chloroform							189	129		343
Carbon Tetrachloride							26	129		
Trichloroethane									215	944
Heavy Chlorinated Compounds									215	
Aromatic Solvent				94 (a)			9 (a)			
Water					552	17,848	69			
Caustic Soda					138					
Sodium Chloride						202				
Hydrogen Chloride		66,942								
Total, Lbs./Hr.	27,250	67,286	90,830 (c)	78,588	690	18,050 (b)	1,170	635	645	87,071

(a) Only present if aromatic solvent is used for product recovery.

(b) If waste water stripper is not provided, stream will also contain EDC (50 lbs./hr.) and light chlorinated hydrocarbons (85 lbs./hr).

(c) One plant (52-10) uses tonnage oxygen in place of air.

average air emission and product composition data derived from plant survey questionnaires and do not represent actual data from any specific plant or process. Feed requirements were determined by carbon and chlorine material balance. It should be noted that the resulting ethylene feed requirement as shown in Tables ED-1 and 1A is three to four more percent than reported in the plant surveys and published articles.[1,3] Slight material balance differences can be explained by the fact that most operators choose an economical operating point which represents the lowest total cost of all materials used. Generally, more complete conversion of HCl can be achieved by using somewhat more than the minimum ethylene quantity. Some plants may, therefore, prefer to optimize HCl consumption at the expense of a small increase in ethylene feed. Beyond this optimization of raw material, feed usage depends largely on the efficiency of the reactor control system.

Table ED-2 presents an estimated heat balance around the oxychlorination reactor system.

TABLE ED-1A
TYPICAL MATERIAL BALANCE FOR PRODUCING ETHYLENE DICHLORIDE BY OXYCHLORINATION PROCESS

Component	1 Ethylene	2 Hydrogen Chloride	3 Air	4 Process Vent Gas	5 Dilute Caustic	6 Combined Waste Water	7 Distillation Vent Gas	8 Chlorinated By-Product	9 Heavy Ends	10 EDC Product
Carbon Dioxide				0.0246						
Carbon Monoxide				0.0068						
Nitrogen			0.8122	0.8115			0.0007			
Oxygen			0.2467	0.0456						
Methane		0.0020		0.0020						
Ethylene	0.3173			0.0049			0.0001			
Ethane	0.0003	0.0020		0.0067			0.0002			
Ethylene Dichloride				0.0070			0.0045	0.0037	0.0025	1.0000
Ethyl Chloride				0.0060			0.0020	0.0003		
Vinyl Chloride							0.0002			
Dichloroethylene							0.0025	0.0004		
Chloroform							0.0022	0.0015		0.0040
Carbon Tetrachloride							0.0003	0.0015		
Trichloroethane									0.0025	0.0110
Heavy Chlorinated Compounds									0.0025	
Aromatic Solvent				0.0011 (a)			0.0001 (a)			
Water					0.0064	0.2080	0.0098			
Caustic Soda					0.0016					
Sodium Chloride						0.0023				
Hydrogen Chloride		0.7803								
Total, Tons/Ton EDC	0.3176	0.7843	1.0589 (c)	0.9162	0.0080	0.2103 (b)	0.0136	0.0074	0.0075	1.0150

(a) Only present if aromatic solvent is used for product recovery.

(b) If waste water stripper is not provided, stream will also contain EDC (0.0006 T/T) and light chlorinated hydrocarbons (0.001 T/T).

(c) One plant (52-10) uses tonnage oxygen in place of air.

TABLE ED-2
OXYCHLORINATION REACTOR SYSTEM
HEAT BALANCE*

Heat Out		BTU/Lb. of EDC
Steam Generation		1,214
Reactor Heat Losses		6
Quench plus Effluent Cooling (575 - 100 °F)		609
Incremental Effluent Heat Content**		-284
	Total	1,545
Heat In		
Exothermal Heat of Reaction		
Ethylene Dichloride Formation		1,383
Effluent Neutralization		2
Feed Vaporization and Preheat		160
	Total	1,545

*Basis

1) Table ED-1A material balance.
2) Feed preheated to 300 °F.
3) Reactor outlet temperature 575 °F.

**Difference in heat content of effluent @ 100 °F and ethylene feed @ 40 °F (liquid) plus air and anhydrous HCl @ 100 °F.

III. Manufacturing Plants and Emissions

Table ED-3 presents a list of U. S plants producing ethylene dichloride. This table also shows published [2,7] capacity figures for these units. Approximately 80% of the total plant capacity is located in Texas and Louisiana with the remaining production in Kentucky and California. These EDC plants are built within 1 to 5 miles of towns and cities with population ranging between 2,000 and 360,000. The type of process is noted in the table.

Table ED-3A shows individual plant capacity figures and emission data for all of the U. S. plants producing EDC by the oxychlorination process. Emissions from these plants are as follows:

A. Continuous Air Emissions

1. Main Process Vent Gas

This stream, which generally vents from a scrubber or an absorber, consists of the gross reactor effluent after quenching and trim cooling for recovery of EDC. The process vent gas emissions presented in Table ED-3A are average values, with the actual composition depending on catalyst activity and reactor operating conditions. Table ED-4 shows a typical breakdown of components in this stream, which represents the primary air emission in the oxychlorination process.

In addition to catalyst activity and reactor operating conditions, the specific processing scheme employed has some influence on the amount of vent gas emissions. For example, in one process, chlorine is added downstream of the main oxychlorination reactor in order to convert unreacted ethylene to EDC. By using chlorine for clean-up, it is not essential to obtain maximum conversion in the oxychlorination reactors. This permits a reduction in the amount of excess air employed and also results in a significant reduction in emissions. According to the survey data, hydrocarbon emissions in the vent gas stream are about half as much as those indicated for plants incorporating several other air oxychlorination processes. In the plants that have chlorine addition (52-7, 52-8 and 52-9), the process vent gas is sent to a water or dilute caustic scrubber for removal of HCl (up to 0.0004 T/T EDC) and unreacted chlorine (about 0.0002 T/T EDC) before emitting this stream to the atmosphere.

In some of the other air oxychlorination plants (52-4, 52-5 and 52-6), an absorber-stripper system is used to recover additional chlorinated hydrocarbons from the process vent gas. In these units, a small amount of absorption oil (aromatic solvent) is lost in the atmospheric vent (0.0011 T/T EDC). However, total hydrocarbon emissions are similar to the chlorine addition plants (0.015 T/T EDC).

The main process vent gas emissions shown in Tables ED-1 and ED-4 approximate a weighted average (based on EDC capacity) of emissions from all surveyed air oxychlorination plants. Since about 65% of the air oxychlorination EDC is produced in plants that incorporate absorber-stripper or chlorine clean-up systems, the emissions shown in these tables do not truly represent actual values obtained in any specific plant. In other words units with chlorine addition or lean oil absorption systems would tend to have lower losses than shown for the "typical unit". Whereas, plants with minimum clean-up facilities would have a somewhat higher level of emissions.

TABLE ED-3
SUMMARY OF U. S. ETHYLENE DICHLORIDE PLANTS

Company	Location	Published Capacity, MM Lbs./Yr. [a]	Process
Allied Chemical Corp.	Baton Rouge, La.	850	Balanced [b]
American Chemical Co.	Long Beach, Calif.	325	Balanced [b]
Conoco Chemicals	Lake Charles, La.	1,000	Balanced [b]
Diamond Shamrock Chemical Co.	Deer Park, Texas	260	Balanced [b]
Dow Chemical Co.	Freeport, Texas	1,100	Balanced [b]
Dow Chemical Co.	Plaquemine, La.	1,160 [c]	Balanced [b]
Ethyl Corporation	Baton Rouge, La.	550	Balanced [b]
Ethyl Corporation	Houston, Texas	260	Direct Chlorination
The B. F. Goodrich Co.	Calvert City, Ky.	1,600	Balanced [b]
PPG Industries, Inc.	Lake Charles, La.	1,000	Balanced [b]
Shell Chemical Co.	Deer Park, Texas	1,700	Balanced [b]
Union Carbide Corp.	Taft, La.	150	Acetylene & HCl
Union Carbide Corp.	Texas City, Texas	150	Acetylene & HCl
Vulcan Materials Co.	Geismar, La.	240	Oxychlorination
		10,345	

(a) There are some discrepancies between actual and published capacity figures.

(b) Includes both direct and oxychlorination units.

(c) Oxychlorination facility presently not in operation.

TABLE ED-3A
SURVEY OF U. S. OXYCHLORINATION PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Plant Code Number	52-1		52-2	
Date on-stream	1968			
Capacity, Tons of Ethylene Dichloride/Yr.	236,350		130,000	
Average Production, Tons EDC/Yr.			130,000	
Range in Production, % of Max.	No seasonal variation		No seasonal variation	
By-products, Tons/Yr.				
Mixed Chlorinated HC				
Emissions to Atmosphere				
Stream	Process Vent	Distillation Vent	Process Vent	
Flow (a), Lbs./Hr.	45,000	1,700	36,100	
Flow Characteristics	Continuous	Continuous	Continuous	
if Intermittent, Hrs. of Flow/Yr.				
Composition, T/T EDC				
Particulate				
Carbon Dioxide	0.032		0.034	
Carbon Monoxide	0.008		0.008	
Nitrogen	0.710	0.0003 (c)	1.048	
Oxygen	0.018		0.007	
Methane	0.011	0.00001		
Ethylene	0.006	0.00003	0.002	
Ethane	0.033	0.0002	0.009	
Ethylene Dichloride	0.012	0.0077	0.004	
Mono & Dichloroacetylene				
Ethyl Chloride	0.008	0.0062		
Vinyl Chloride		0.0007		
Dichloro Ethylene		0.0080		
Chloroform		0.0064		
Carbon Tetrachloride		0.0010		
Water		0.0008		
Aromatic Solvent				
Chlorine				
Hydrogen Chloride				
Sample Tap Location	Before & after contact condenser	Accessible	Accessible	
Date or Frequency of Sampling	Continuous for O_2, CO_2 & $C_2^=$, other HC's once per day, CO 6 times/Yr.	4 times/Yr.	Orsat 6/day, G.C. 1/wk.	
Type of Analysis	G.C.	G.C.	Orsat & G.C.	
Odor	None	Not beyond plant boundary	None	
Color				
Vent Stacks				
Number	1	1	1	
Height	50'	10'	27'6"	
Diameter	1'0"	6"	8"	
Exit Gas Temp., °F	32	80	80	
SCFM per Stack (a)	9,900	135	8,000	
Type of Emission Control	Contact Condenser		Condenser (-10 °F)	
Date Installed	1968			
Total Emissions, Ton/Ton EDC				
Hydrocarbons	0.088		(n)	
Particulates & Aerosols (b)	0.001		0.015	
NO_x				
SO_x				
CO	0.008		0.008	

TABLE ED-3A CONT'D.
SURVEY OF U. S. OXYCHLORINATION PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Plant Code Number	52-3			
Date on-stream	1968			
Capacity, Tons of Ethylene Dichloride/Yr.	115,000			
Average Production, Tons EDC/Yr.	115,000			
Range in Production, % of Max.	No seasonal variation			
By-products, Tons/Yr.				
Mixed Chlorinated HC				
Emissions to Atmosphere Stream	Process Vent	Caustic Scrubber Vent	Drying Tower Ovh'd.	Emergency Vent
Flow (a), Lbs./Hr.	18,300	90	12	8,200
Flow Characteristics	Continuous	Continuous	Continuous	Intermittent
If Intermittent, Hrs. of Flow/Yr.				6
Composition, T/T EDC				
Particulate	0.010			
Carbon Dioxide	0.005	0.00001	0.00001	0.0045
Carbon Monoxide	0.604	0.00003	0.00002	0.0023
Nitrogen	0.019	0.00118	0.00007	0.2652
Oxygen		0.00008	0.00001	0.0085
Methane	0.005			
Ethylene	0.008	0.00012	0.00016	0.0020
Ethane	0.017	0.00015	0.00017	0.0034
Ethylene Dichloride		0.00144		0.0076
Mono & Dichloroacetylene	0.011			
Ethyl Chloride		0.00014		0.0049
Vinyl Chloride		0.00001		
Dichloro Ethylene		0.00001		
Chloroform		0.00002		
Carbon Tetrachloride		0.00003		
Water				
Aromatic Solvent				
Chlorine				
Hydrogen Chloride				
Sample Tap Location	TR (e)	0.00009		0.0004
Date or Frequency of Sampling	None after scrubber, accessible tap before scrubber	No problem	Accessible	Accessible
	Scrubber feed 3-6 times/yr.	Twice in Dec. 1971	Not as yet (f)	4 times recently
Type of Analysis	G.C.	G.C.		G.C.
Odor	Occasional HCl	None	None	HCl within battery limits
Color				
Vent Stacks	1	1	1	1
Number	76'	49'	72'	79'
Height	1'	2"	2"	7"
Diameter	80	100	60	40
Exit Gas Temp., °F	3,980	13	2.6	2,000
SCFM per Stack (e)	Scrubber		Condenser	
Type of Emission Control	1968 - 1971		1972	
Date Installed				
Total Emissions, Ton/Ton EDC				
Hydrocarbons		0.044		
Particulates & Aerosols (b)				
NO_x				
SO_x		0.005		
CO				

TABLE ED-3A CONT'D.
SURVEY OF U. S. OXYCHLORINATION PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Plant Code Number	52-4			52-5			
Date on-stream				1963			
Capacity, Tons of Ethylene Dichloride/Yr	107,500						
Average Production, Tons EDC/Yr.				330,000			
Range in Production, % of Max.	2nd quarter 20% below ave. 4th " " above ave.			No seasonal variation			
By-products, T/T EDC							
Mixed Chlorinated HC				0.0075 (j)			
Emissions to Atmosphere							
Stream	Absorber Vent	Absorber Vent	Absorber Vent	Waste Water Stripper Ovh'd.	Waste Water Stripper Ovh'd.	Heads Column Vent	
Flow (a), Lbs./Hr.	33,800	71,000	31,000	77	25	120	
Flow Characteristics	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	
If Intermittent, Hrs. of Flow/Yr.							
Composition, T/T EDC							
Particulate							
Carbon Dioxide	0.048	0.025	0.005	X	X	X	
Carbon Monoxide	0.012	0.006	0.002				
Nitrogen	1.025	0.748	0.350	X	X	X	
Oxygen	0.100	0.071	0.033	X	X	X	
Methane	0.038	0.008	0.004				
Ethylene	0.006	0.004	0.002				
Ethane		0.001	0.001				
Ethylene Dichloride	0.022 (i)	0.002	0.0003	0.00003	0.00005	0.0002	
Mono & Dichloroacetylene							
Ethyl Chloride				0.00036	0.00005	0.0006	
Vinyl Chloride							
Dichloro Ethylene							
Chloroform							
Carbon Tetrachloride							
Water				0.000006	0.000002	0.00001	
Aromatic Solvent	0.0004	0.0005	0.0002				
Chlorine							
Hydrogen Chloride							
Sample Tap Location	Piped to continuous analyzer	Accessible	Accessible	None	None	None	
Date or Frequency of Sampling	Every 13 minutes	4 per hour	4 per hour	Never sampled	Never sampled	Never sampled	
Type of Analysis	G.C.	G.C.	G.C.	None	None	None	
Odor	None	No problem	No problem	No problem	No problem	No problem	
Color							
Vent Stacks							
Number	1	1	1	1	1	1	
Height	175'	150'	150'	40'	50'	150'	
Diameter	8"	1'0"	1'2"	2"	3"	2"	
Exit Gas Temp., °F	50	65	70	55	55	55	
SCFM per Stack	7,500	15,900	6,950	12.5	5	17	
Type Emissions Control		Demister	Demister	Refrig. Cond.	Refrig. Cond.	Refrig. Cond.	
Date Installed		1963	1967	1963	1967	1966	
Total Emissions, Ton/Ton EDC	(n)						
Hydrocarbons	0.028			0.011			
Particulates & Aerosols (b)							
NO_x							
SO_x							
CO	0.012			0.008			

TABLE ED-3A CONT'D.
SURVEY OF U. S. OXYCHLORINATION PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Plant Code Number	52-6			
Date on-stream	1960			
Capacity, Tons of Ethylene Dichloride/Yr.	85,000			
Average Production, Tons EDC/Yr.	1st quarter 20% below ave. 2nd " " above ave.			
Range in Production, % of Max.				
By-products, T/T EDC				
Mixed Chlorinated HC				
Emissions to Atmosphere				
Stream	Absorber Vent	Stripper Vent	Heede Column Vent	Emergency Vent
Flow [a], Lbs./Hr.	21,200	245	120	22,200
Flow Characteristics	Continuous	Continuous	Continuous	Intermittent
If Intermittent, Hrs. of Flow/Yr.				180
Composition, T/T EDC				
Particulate	Nil			Nil
Carbon Dioxide	0.047			
Carbon Monoxide	0.013			
Nitrogen	0.875	0.0004	0.0028	1.0383 [d]
Oxygen	0.069			
Methane				
Ethylene	0.008			
Ethane				
Ethylene Dichloride	0.003	0.0029	0.0002	0.0762
Mono & Dichloroacetylene				
Ethyl Chloride	0.002 [c]			0.0001 [k]
Vinyl Chloride				
Dichloro Ethylene			0.0023	
Chloroform				
Carbon Tetrachloride				
Water	0.009	0.0083	0.0004	0.0811
Aromatic Solvent	0.003		0.0001	0.0011
Chlorine				
Hydrogen Chloride				
Sample Tap Location	Piped to continuous analyzer	None	None	None
Date or Frequency of Sampling	O_2 - Continuous, Others every 13 min.	Never sampled	Never sampled	Never sampled
Type of Analysis	Ethylene continuous			
Odor	G.C. + IR for ethylene	None	None	None
Color	None	None	None	None
Vent Stacks				
Number	1	1	1	1
Height	65'	35'	35'	50'
Diameter	6"	4"	2"	8"
Exit Gas Temp., °F	55	100	100	50
SCFM per Stack	4,660	67	18.5	4,780
Type Emissions Control	Demister & Separator			
Date Installed	1968			
Total Emissions, Ton/Ton EDC				
Hydrocarbons		0.020		
Particulates & Aerosols [b]		Nil		
NO_x				
SO_x				
CO		0.013		

TABLE ED-3A CONT'D.
SURVEY OF U. S. OXYCHLORINATION PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Plant Code Number	52-7	52-8	52-9
Date on-stream	1971		
Capacity, Tons of Ethylene Dichloride/Yr.	287,000	246,000	50,000
Average Production, Tons EDC/Yr.			
Range in Production, % of Max.			
By-products, T/T EDC			
Mixed Chlorinated HC			
Emissions to Atmosphere			
Stream	Process Vent	Process Vent	Process Vent
Flow [a], Lbs./Hr.	45,200 [1]	36,200 [1]	7,700 [1]
Flow Characteristic	Continuous	Continuous	Continuous
If Intermittent, Hrs. of Flow/Yr.			
Composition, T/T EDC			
Particulate			
Carbon Dioxide	0.008	0.007	0.008
Carbon Monoxide	0.004	0.004	0.004
Nitrogen	0.579	0.541	0.566
Oxygen	0.025	0.023	0.024
Methane			
Ethylene	0.004	0.004	0.004
Ethane			
Ethylene Dichloride	0.004	0.004	0.004
Mono & Dichloroacetylene			
Ethyl Chloride	0.005	0.005	0.005
Vinyl Chloride			
Dichloro Ethylene			
Chloroform			
Carbon Tetrachloride			
Water			
Aromatic Solvent			
Chlorine	0.0002	0.0001	0.0002
Hydrogen Chloride			
Sample Tap Location	Inconvenient	Inconvenient	Inconvenient
Date or Frequency of Sampling	Scrubber Feed - Continuous Scrubber Vent - Continuous for Cl_2	Scrubber Feed - Continuous Scrubber Vent - Very Infrequent	Scrubber Feed - Continuous Scrubber Vent - Very Infrequent
Type of Analysis	G.C. & Ultraviolet Spec.	G.C.	G.C.
Odor			
Color			
Vent Stacks	Not beyond plant boundary - Cl_2 & HCl [m]	Not beyond plant boundary - Cl_2 & HCl [m]	Not beyond plant boundary - Cl_2 & HCl [m]
Number	1	1	1
Height	≈ 135'	≈ 135'	≈ 75'
Diameter	30"	30"	18 - 24"
Exit Gas Temp., °F	Ambient	Ambient	Ambient
SCFM per Stack [a]	10,000 [1]	3,000 [1]	1,700 [1]
Type of Emissions Control	Water Scrubber	Water Scrubber	Water Scrubber
Date Installed			
Total Emissions, T/T EDC			
Hydrocarbons	[n]	[n]	[n]
Particulates & Aerosols [b]	0.013	0.013	0.013
NO_x			
SO_x			
CO	0.004	0.004	0.004

TABLE ED-3A CONT'D.
SURVEY OF U. S. OXYCHLORINATION PLANTS
AND ATMOSPHERIC EMISSIONS FROM THESE FACILITIES

Plant Code Number	52-10		
Date on-stream	1967		
Capacity, Tons of Ethylene Dichloride/Yr.	118,625		
Average Production, Tons EDC/Yr.	118,625		
Range in Production, % of Average	No seasonal variation		
By-products, T/T EDC			
Mixed Chlorinated HC			
Emissions to Atmosphere			
Stream	Process Vent		Emergency Vent
Flow (a), Lbs./Hr.	1,450		
Flow Characteristics	Continuous		Intermittent
If Intermittent, Hrs. of Flow/Yr.			
Composition, T/T EDC			
Particulate			
Carbon Dioxide	0.0119		
Carbon Monoxide			
Nitrogen	0.0167		X
Oxygen			
Methane			
Ethylene	0.0128		
Ethane	0.0002		
Ethylene Dichloride	0.0065		
Mono & Dichloroacetylene	0.0007		
Ethyl Chloride	0.0033		
Vinyl Chloride	0.0007		
Dichloro Ethylene	0.0002		
Chloroform	0.00004		
Carbon Tetrachloride			
Water	0.0006		
Aromatic Solvent			
Chlorine			
Hydrogen Chloride			
Sample Tap Location	Vent under vacuum		(g)
Date or Frequency of Sampling	Fall of 1971		Can be done Never Sampled
Type of Analysis	G.C.		
Odor			
Color			
Vent Stacks	EDC within battery limits		None
Number		1	
Height		75'	
Diameter		8"	
Exit Gas Temp., °F		75	
SCFM per Stack	260		1000 (h)
Type Emissions Control	Scrubber		Scrubber
Date Installed	1967		1967
Total Emissions, Ton/Ton EDC			
Hydrocarbons		(e)	
Particulates & Aerosols (b)		0.024	
NO_x			
SO_x			
CO			

TABLE ED-3A FOOTNOTES

(a) Based on average production rate if available, otherwise based on design capacity.

(b) Includes HCl and carbon tetrachloride.

(c) Air.

(d) Includes oxygen.

(e) Normal feed to scrubber contains 0.0008 tons HCl/ton EDC. However, during reactor start-up (max. 30 min., 24 times per year), feed can contain as much as 0.50 tons HCl/ton EDC. During emergency conditions such as power failure, when scrubber becomes ineffective, most of this HCl will be vented to the atmosphere. Duration is normally 3 - 5 minutes required to secure plant.

(f) Recovery unit not put in operation until after plant survey.

(g) During start-up, feed to scrubber contains 0.163 tons of nitrogen per ton of EDC production capacity and 0.106 tons of HCl per ton of EDC. Duration is approximately 20 minutes. During emergency venting, the vent contains a small amount of organic material.

(h) Represents nitrogen flow during start-up.

(i) Absorber-stripper may shut down for undetermined period during which time EDC content in vent increases to three times value shown.

(j) Sent to off-site disposal plant.

(k) Includes methane and ethane.

(l) Represents normal flow from EDC unit. Actual total vent from stack includes streams from other units in VCM plant. Vent gas composition shown is based on analysis of scrubber feed gas from EDC oxychlorination unit. It has been assumed that water scrubber removes contained HCl (0.00004 T/T EDC).

(m) Only during plant upset.

(n) Survey data does not include information regarding air emissions resulting from EDC purification.

It should be noted that flow rates and compositions shown for intermittent streams represent emissions during flowing condition and not yearly averaged values. The total plant emission figures shown are averaged emissions for extended periods of operation.

TABLE ED-4
TYPICAL VENT GAS COMPOSITION (a)
FOR
700 MM LB./YR. ETHYLENE DICHLORIDE PRODUCTION
BY OXYCHLORINATION PROCESS

Component	Normal Range in Composition Mol. %	Average Flow Rate MPH	Lbs./Hr.
Carbon Dioxide	0.8 - 3.5	47.9	2,110
Carbon Monoxide	0.6 - 1.3	20.8	583
Nitrogen	82 - 95	2,484.4	69,612
Oxygen	0.5 - 7.5	122.3	3,912
Methane	0 - 5.0 (c)	10.7	172
Ethylene	0.2 - 0.8	15.0	420
Ethane	0 - 3.8 (d)	19.1	575
Ethylene Dichloride	0.07 - 0.75	6.1	600
Ethyl Chloride	0 - 0.75	7.9	510
Aromatic Solvent (b)	0 - 0.1	0.9	94
		2,735.1	78,588

(a) Downstream of water or caustic scrubber facilities. Prior to scrubbing operations, stream normally contains about 65 lbs./hr. HCl (0.0007 T/T of EDC production).

(b) Only present if aromatic solvent is used for product recovery. (Plants 52-4, 52-5 & 52-6.)

(c) Only present in plants 52-1, 52-4, and 52-5. This represents methane impurity contained in ethylene and HCl reactor feed.

(d) Primarily represents saturate impurity in ethylene feed.

In the one U. S. oxychlorination plant using tonnage oxygen in place of air (52-10), total vent gas emissions are greatly reduced. However, hydrocarbon emissions for this unit are similar to those shown in Table ED-4.

There are no odor problems associated with the main process and other vent streams. In some instances, especially during plant start-up, odors from HCl, Cl_2 or chlorinated hydrocarbons are detected on-site but these do not permeate beyond the plant boundary.

2. Product Fractionation Vent

This normally represents a small stream, which varies greatly in composition, depending upon the type of fractionation system used for product recovery and the desired product purity. In most plants no product fractionation facilities are provided on-site. In these units the crude EDC is either combined with products from other plants for clean-up or impurities are rejected in downstream vinyl chloride monomer facilities.

In some cases, this stream consists of the combined vent from several fractionators.

3. Product Storage Losses

Because of low EDC vapor pressure at ambient temperature (3 PSI @ 100° F), product storage tanks are directly vented to the atmosphere, usually with nitrogen padding. Some plants use conservation type vents to reduce emissions while filling. Based upon average tank turnaround figures, it is estimated that EDC losses from stroage facilities equals about 0.0006 T/T EDC production.

4. Waste By-Product Disposal

Heavy chlorinated by-products removed in the product fractionation section are normally sent to an incinerator. Light chlorinated compounds produced in the process can be used as supplemental feed in manufacture of perchloro-ethylene and carbon tetrachloride or fractionated for recovery of specific fractions or compounds. However, in some locations where there is little or no market demand for this material, both by-product streams are incinerated. Plant (52-5) burns this material plus chlorinated hydrocarbon waste products from other processing units in an off-site incinerator. Effluent from the incinerator is cooled and sent to absorbers for recovery of HCl. Unrecovered HCl and any chlorine formed in the incineration are removed in a dilute caustic scrubber before atmospheric venting of the effluent.

B. Intermittent Air Emissions

During reactor start-ups (10 - 20 minutes duration about twice a month) feed to the process vent gas water or dilute caustic scrubbers contains between 0.10 to 0.5 tons HCl/ton EDC. Normal feed to scrubber contains approximately 0.0005 tons HCl/ton EDC. During emergency conditions such as power failure, when scrubber becomes ineffective, this HCl will be vented to the atmosphere. At least one oxychlorination process requires a catalyst conditioning step, which results in some ethylene emission during reactor start-up operations.

C. Liquid Wastes

Water condensed from the reactor effluent plus spent caustic from the neutralizer represent the primary liquid waste streams. The combined flow of these two streams varies substantially from plant to plant (0.2 to 1.4 T/T EDC). In one unit (52-5), waste water strippers are provided on-site to recover contained EDC and light chlorinated hydrocarbons (0.0016 T/T EDC). In all other units, this water is sent off-site for treatment or used for pH control in other processing areas.

D. Solid Wastes

Approximately 0.0002 T/T EDC of solid wastes are removed from the reject water settling ponds in plants that use fluidized bed reactors. These solids are catalyst particles scrubbed from the reactor effluent. Plants with fixed bed reactors do not have solid wastes, except intermittently when an entire catalyst charge is replaced.

E. Fugitive Emissions

All but one plant surveyed report that fugitive emissions are minor. The one plant that estimated losses reported that total storage tank vents plus fugitive emissions are about 0.01 T/T EDC production. Based upon the comments provided by the other respondents, this loss figure appears high.

It is logical to conclude that due to the nature of the chlorinated hydrocarbons involved, the plant operators would be careful in their maintenance and sampling in order to minimize fugitive losses.

IV. Emission Control Devices and Systems

A. Main Process Vent Gas Stream

1. Devices Currently Employed

(a) Scrubbers

At present most U.S. plants that do not have an aromatic solvent absorber-stripper system for product recovery employ a water or dilute caustic scrubber on this vent stream, see Table ED-5. The scrubber is used to remove small amounts of HCl (approximately 0.0008 T/T EDC) and, in some cases, chlorine (0.0002 T/T EDC) left in the non-condensed reactor effluent.

Water scrubbing is sufficient for removing HCl. However, if chlorine is present, dilute caustic is required for efficient operation.

In many of the units that do not have vent gas scrubbers, HCl is removed in the gross reactor effluent water quench or caustic scrubbing facilities.

(b) Contact Condenser

One plant (52-1) passes the vent gas through a direct contact condenser. Whereas the above scrubbers are primarily used to remove HCl, the contact condenser is employed to recover EDC (0.02 T/T EDC product) and other light chlorinated hydrocarbons (0.002 T/T EDC).

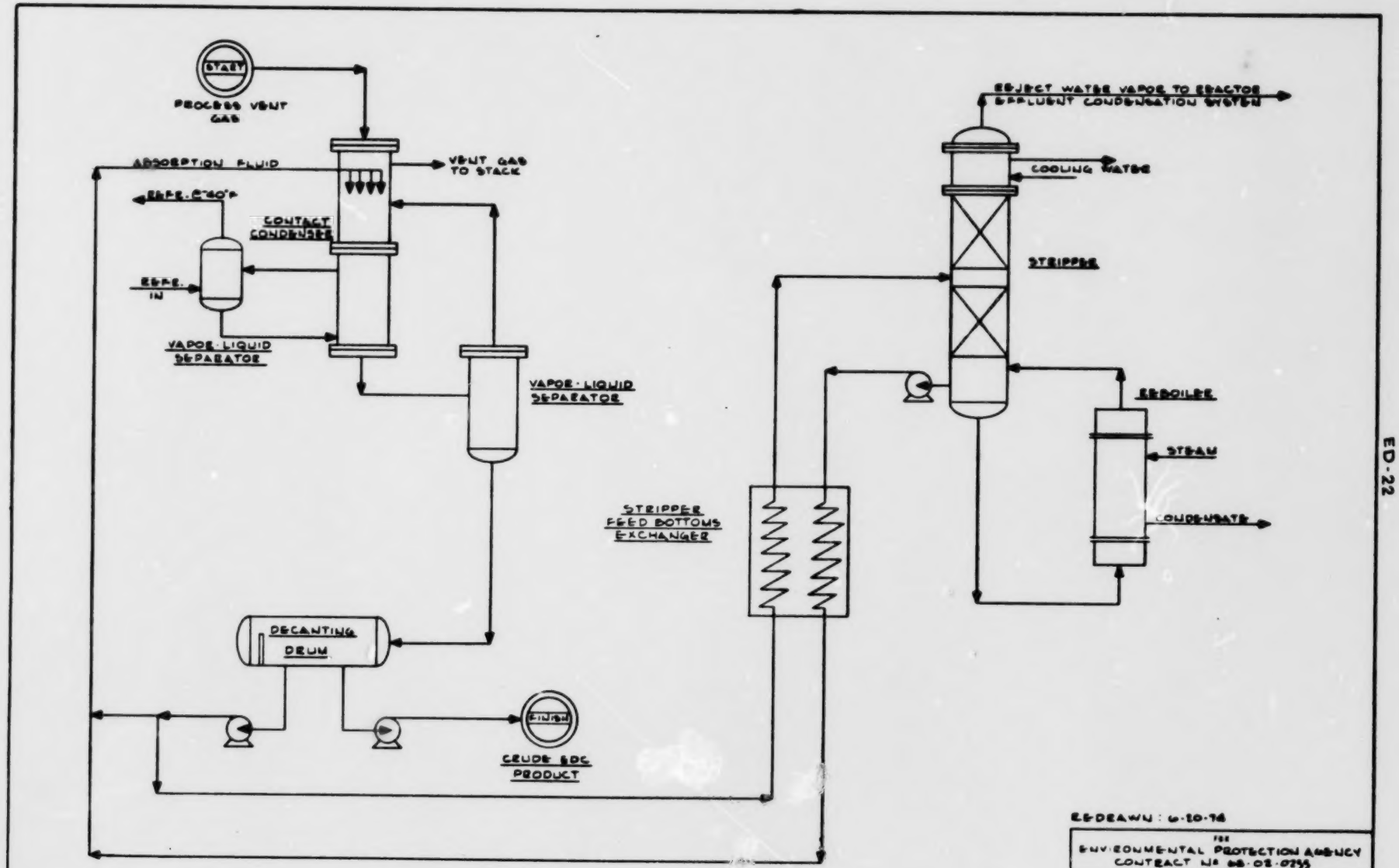
Figure ED-2 presents a simplified flow diagram for the vent gas contact condenser system. Process vent gas is fed to the tube side of two shell and tube heat exchangers operated in series. In the first exchanger the gas is contacted with an unnamed absorption fluid and indirectly cooled with processed vent gas. In the second exchanger, refrigerant is used to further cool the mixture. Liquid chlorinated hydrocarbons plus absorption fluid are removed from the exchanger effluent in a vapor-liquid separator. A decanting drum is used to separate EDC from the absorption fluid. The recovered EDC (90 wt. percent EDC) is combined with reactor effluent liquid for water washing and product distillation. The circulating absorption fluid stream is sent to a stripper tower for removal of water. Maloperation of stripper occasionally results in water recycle and condenser freeze-up.

Based upon overall hydrocarbon emissions shown in Table ED-3A, it would appear that the above contact condenser system is not a very efficient air pollution control device. However, in this case, the emission data are misleading, Plant 52-1 processes recycled gas streams from other processing units in order to utilize contained raw materials. This results in carbon dioxide and light hydrocarbon impurities being charged to the oxychlorination reactors (feed contains 82-92 wt. percent ethylene versus 99.9 wt. percent for other plants). Most of these impurities are rejected in the main process vent stream.

Since plant 52-1 apparently cools the vent stream to

TABLE ED-5
PROCESS VENT GAS SCRUBBERS
FOR
OXYCHLORINATION PLANTS

Plant Code Number	52-3	52-7	52-8	52-9	52-10	
Operation	Continuous	← Continuous →			Continuous	Intermittent (Emergency)
Purpose - Control Emission of	HCl	← HCl & Cl_2 →			HCl	HCl
Type of Scrubber						
Spray					X	X
Packed Column - Type of Packing	3" intalox saddles					
Bed Depth	5'0"					10'0"
Other		← Not Specified →				
Scrubbing Liquid	Water	← Dilute caustic or water →			Water	Water
Flow Rate, GPM	15	1,200	1,200	Not Specified	10	45
Feed Gas						
Flow Rate, SCFM	3,980	10,000	8,000	1,700	260 normal, 650 (max.)	4,500 (max.)
Temperature, °F		← Atmospheric →				
Pressure, PSIG	Atmos.				Atmos.	Atmos.
Scrubber ΔP	0.95 in. H_2O					
Tower Dimensions						
T-T Height	16'0"	25'0"	25'0"	Not specified	16'0"	17'0"
Diameter, ID	4'6½"	10'10"	10'10"	" "	1'4"	3'6"
Washed Gases to Stack	Yes	Yes	Yes	Yes	Combined vent to single stack	
Temperature, °F	80	Ambient	Ambient	Ambient	75	
Stack Height (above grade)	76'	135'	135'	75'	75'	
Stack Diameter	1'0"	2'6"	2'6"	18" - 24"	8"	
Date Installed	1968 - 1971	1971			1967	1967
Installed Cost - Material & Labor - $	116,500	300,000	300,000	Not specified	5,400	12,600
Installed Cost - ¢/lb. of EDC/Yr.	0.0514	0.0522	0.0610	" "	0.0023	0.0053
Operating Cost - Annual - $	16,500	75,000	75,000	" "	> 200	> 400
Operating Cost - ¢/lb. of EDC	0.0073	0.0131	0.0152	" "	0.0001	0.0002
Efficiency - %	Not specified	100	100	100	100	Not specified
Comments	Scrubber feed is precooled in direct contact condenser 3'8" OD x 16' containing 596 1½" Impervite tubes. Water circulation = 100 GPM Above cost data include this equipment.	In addition to process vent gas flow rates shown, scrubbers handle other vent streams from the associated vinyl chloride plants. Cost figures shown represent total cost of the scrubbing facilities. According to respondents report, it is not practical to apportion the capital cost of this device among the various users. Efficiency figures are based on using dilute caustic in scrubber. If only water is employed, vent gas will contain about 100 PPM chlorine.				



ED-22

EDRAWN: 6-20-74

SCALE	NONE	DATE
DRAWN BY	D H	5-24-74
CHECKED BY	R C B	7-2-74
APPROVED		

FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO 68-02-0799

PREPARED BY
CATALYTIC, INC.
ENGINEERING DEPARTMENT, PHILADELPHIA, PENNA.

FIGURE ED-2
SIMPLIFIED FLOW DIAGRAM
PROCESS VENT GAS
EDC RECOVERY SYSTEM

JOB NO	DWG NO	REV NO
42030	E-223	A
CO NO 510		

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a colder temperature than most other plants, it is assumed that similar amounts of chlorinated hydrocarbons would be liquefied and recovered in this facility as with other currently used control devices processing the same vent gas.

(c) Refrigerated Condensers

One plant (52-2) passes the vent stream through two stages of refrigeration, which cool the gas to -10° F for recovery of chlorinated hydrocarbons. Specific data regarding the condenser system and amount of material recovered are not available. However, net hydrocarbon emissions are low (0.015 T/T EDC).

(d) Mist Eliminators

The plants that incorporate an aromatic solvent absorber-stripper system for product recovery (52-4, 52-5 and 52-6), have a mist eliminator in the absorber to prevent liquid carry over. One unit (52-6) also has a downstream knock out drum for liquid removal before stack venting of the off-gas. It is estimated that these facilities recover approximately 0.01 tons of solvent per ton of EDC production.

2. Combustion Devices (None currently employed)

In order to remove CO and further reduce hydrocarbon emissions in the process vent, one of the following combustion devices could be considered. However, at present none of these devices are used in this service.

(a) Direct Fired Boiler and Scrubber System

A direct fired boiler is an efficient method of oxidizing these contaminates. [illegible]r, the burning of chlorinated hydrocarbons in this, or any other [illegible]bustion device, produces HCl plus some chlorine. In order to prevent pollution of the atmosphere with these compounds, it is desirable to water wash and or caustic scrub the boiler effluent. The HCl content of the gas stream is too low to make HCl recovery practical.

A large amount of steam is presently produced in the reactor system of a conventional oxychlorination plant. Even with this production, the overall facility (including direct chlorination and VCM production) usually consumes a substantial quantity of steam (about 2 lbs./lb. of VCM production[5]). Therefore, in new plants, it is conceivable that steam production resulting from pollution control facilities could be used in the VCM complex.

Table ED-6 presents a typical material balance for a fired boiler and scrubber system operating on the clean-up of a process vent gas. In order to have essentially complete combustion of pollutants, the boiler data are based on an 1800° F combustion zone temperature and 3 mol. % oxygen (Dry Basis) in the effluent. Maximum steam generation is included in order to reduce cost and water requirements for downstream scrubbing facilities.

TABLE ED-6

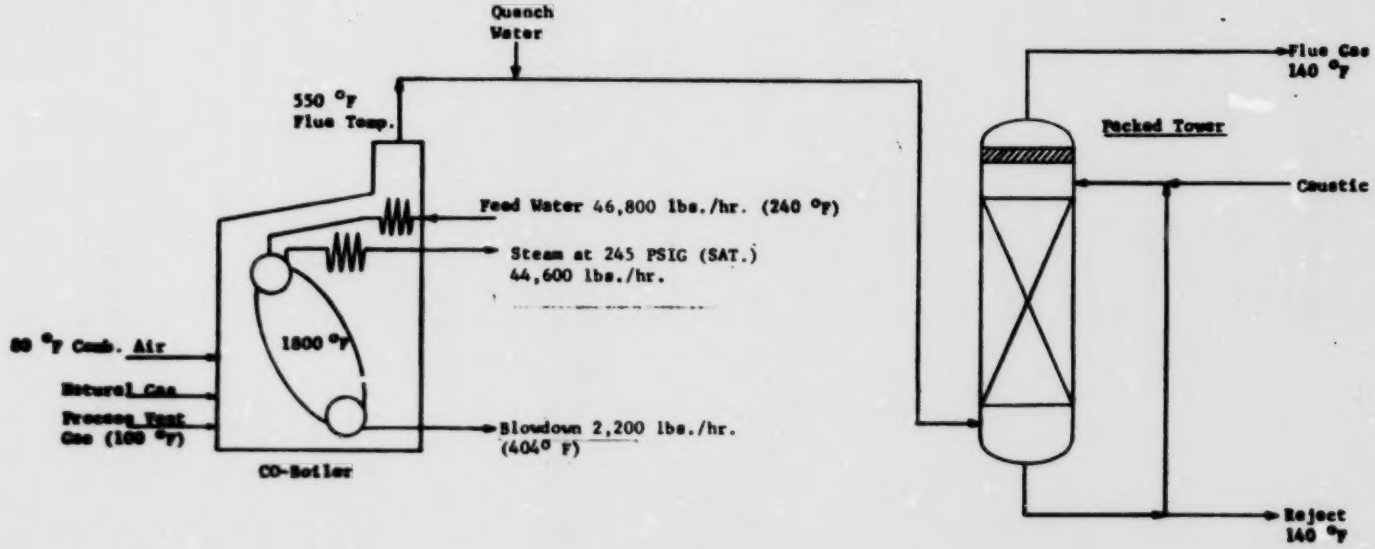
DIRECT FIRED BOILER PLUS SCRUBBER EMISSION CONTROL SYSTEM

FOR

700 MM LB./YR. OXYCHLORINATION PLANT

PROCESS VENT GAS STREAM

	Process Vent Gas	Combustion Air	Natural Gas	Incinerator Flue Gas	Quench Water	Caustic Feed	Scrubber Reject	Scrubber Effluent
Carbon Dioxide	2,110			10,413				10,413
Carbon Monoxide	583							
Nitrogen	69,612	35,334	71	105,016				105,016
Oxygen	3,912	10,732		5,127				5,130
Methane	172		696					
Ethylene	420							
Ethane	575		159					
Ethylene Dichloride	600							
Ethyl Chloride	510							
Aromatic Solvent	94							
Water		608		4,887	36,353		25,127	16,475
Hydrochloric Acid				726				
Chlorine				14				1
Nitrogen Oxides				5				5
Sodium Hydroxide						810		
Sodium Chloride							1,184	
Total Lbs./Hr.	78,588	46,674	926	126,188	36,353	810	26,311	137,040
SCFM	17,280			28,040				31,980



Since none of the surveyed plants use fired boilers or any other combustion device on this vent stream, it is difficult to predict equipment performance in this application. Based upon applications in other areas, the following potential problems exist:

(1) Vent gas is normally available at low pressure

(2) Investment for required blowers, burning equipment and control systems is high.

(3) Effluent stream is corrosive at some conditions.

(4) Because of low heating value (30 to 55 BTU/Ft.^{3}) of the gas stream, up to 45 percent of the total heating value must be added as supplemental fuel in order to achieve complete combustion.

(5) Flame control is difficult and flame-outs may be common due to low heating value and low level of incandescence.

(6) Operating problem results from need to switch to complete fuel gas firing whenever plant emergency necessitates purging the reactor system with nitrogen. This occurs about twice a year.

In similar applications of fired boilers, it has been found that the effluent stream is especially corrosive at temperatures either above 600° F, or below the HCl dew point. In order to maintain steam coils within the non-corrosive temperature range, 245 PSIG saturated steam is assumed to be generated in the boiler and effluent gases are exhausted at 550° F. Adequate instrumentation is required to see that tube wall temperatures do not exceed 600°F or go below 400° F while burning streams containing chlorinated hydrocarbons. Instrumentation is also required for purging chlorinated compounds from the system prior to furnace shutdown.

The boiler effluent is quenched and sent to either a caustic scrubber or combination water-dilute caustic scrubbing unit. The combination unit would be employed if dilute HCl (2-3 wt. % HCl) could be used off-site for stream neutralization or sent to an HCl recovery unit. In the dual scrubbing unit, the gas stream is first contacted with water, which absorbs about 90 percent of the HCl. The gas is then scrubbed with caustic before being discharged to the atmosphere. It is estimated that the stack gases would contain less than one PPM of HCl and 10 PPM by volume of chlorine.

The bottom portion of the scrubbing tower and inlet piping would be lined with fiber reinforced plastics (FRP) or rubber. Porcelain raschig rings, Berl saddles or other types of packing can be used.

Scrubber requirements for processing boiler effluent from the typical 700 MM lbs./yr. oxychlorination unit are as follows:

Type of Scrubber	Combination Unit	Caustic Scrubber
Tower Dimensions, Ft.		
Diameter	11	11
T-T Length	35	25
Water Absorption Section		
Number of Beds	2	
Bed Depth, Ft. (each)	8	
Reject Water Rate, GPM	30	
Wash Water Recirculation Rate, GPM	170	
Bed ΔP, in. of water	2	
Caustic Scrubbing Section		
Number of Beds	1	2
Bed Depth, Ft. (each)	5	8
Spent Caustic Solution*, GPM	5	50
Caustic Recirculation Rate, GPM	195	150
Bed ΔP, Inches of Water	1	2

*contains 4.5 wt. percent NaCl.

The data presented in Table ED-6 and the economics derived therefrom are based on using straight caustic scrubbing without HCl recovery.

(b) Thermal Incineration and Scrubber System

Table ED-7 presents a material balance for this type of control device. Incinerator data are based on the same combustion zone operating conditions used for the direct fired boiler.

Burning of off-gas in a thermal incinerator results in similar burning problems and combustion efficiency anticipated for a direct fired boiler.

Scrubbing data in Table ED-7 and subsequent economics regarding vent gas incineration effluent scrubbing operations are based on using a caustic scrubber similar to that proposed for the direct fired unit.

(c) Incineration plus Steam Generation and Scrubbing System

Table ED-8 presents a material balance and sketch for a thermal incinerator followed by a waste heat boiler and caustic scrubber. This combination facility has an emissions control efficiency and potential similar to that of the direct fired boiler.

There is very little commercial experience of burning chlorinated hydrocarbons in incinerators with steam generation for heat recovery. A Shell Chemical Co. affiliate is reported to have had two 100 percent capacity incinerator and boiler systems processing liquid chlorinated wastes in Europe. On stream factor is believed to have been approximately 25 percent because of brick work deterioration and corrosion problems. This poor performance has resulted in the project being abandoned.

Stauffer Chemical Company has a small fired tube boiler in Bucks, Alabama which burns gaseous chlorinated waste material.[16] This unit, built by John Zink Company, was put in service in August of 1972. After six months operation, it was shut down to replace corroded boiler tubes and tube sheet (carbon steel). Corrosion was attributed to a supplemental feed which contained phosphorous. After retubing one-third of the bundle (carbon steel tubes) and removing phosphorous containing feed, the unit ran for two months before a shutdown was caused by an expansion joint failure between the oxidizer and boiler. The expansion joint had not been packed or insulated and corrosion resulted from condensation during cold weather. Boiler inspection during this shutdown showed no corrosion. Since returning to operation, the unit has run several months with no apparent corrosion problems.

John Zink Company has a pilot unit similar in size to the Stauffer facility.

American Chemical Corporation in Long Beach, California has a thermal oxidizer plus waste heat boiler system for disposal of concentrated gaseous chlorinated hydrocarbons. American Chemical is on its third boiler. The first boiler was water tube and failed within two years. The second was fired tube and lasted five years. The present boiler has been in service two years.

There are reports that there is a B.F. Goodrich licensee in Europe that employs a thermal incinerator plus a carbon steel boiler for heat recovery. This unit has been in operation for two years and is reported to have given satisfactory performance.

Scrubbing data and economics for this system are also based on assumptions made for the direct fired unit.

(d) Submerged Thermal Incineration and HCl Recovery

Submerged exhaust incinerators are primarily used in disposal of waste streams that have a high heating value. The main advantage of this incinerator is that effluent gas can be cooled to acceptable scrubber operating temperature and reject a major portion of the HCl as dilute acid (2-5 wt. % HCl) at relatively low capital expense. However, when dealing with low heating value waste streams such as the process vent gas, a substantial amount of supplemental fuel is required to obtain adequate combustion zone temperature (1800° F). While combustion efficiency for this furnace would be similar to other incinerator systems, overall heat utilization is poor and operating costs would be higher than for the above devices with steam generation.

(e) Catalytic Incinerator

A conventional catalytic incinerator could reduce pollutants to similar levels obtained with a thermal unit. The catalytic facility would operate at lower temperature (800-1000° F) and,

TABLE ED-7
THERMAL INCINERATOR AND SCRUBBER SYSTEM
FOR
700 MM LB./YR. OXYCHLORINATION PLANT
PROCESS VENT GAS STREAM

Component	Process Vent Gas	Combustion Air	Natural Gas	Incinerator Flue Gas	Quench Water	Caustic	Scrubber Reject	Scrubber Effluent
Carbon Dioxide	2,110			10,413				10,413
Carbon Monoxide	583							
Nitrogen	69,612	35,334	71	105,017				105,017
Oxygen	3,912	10,732		5,127				5,130
Methane	172		696					
Ethylene	420							
Ethane	575		159					
Ethylene Dichloride	600							
Ethyl Chloride	510							
Aromatic Solvent	94							
Water				4,887	75,812		25,127	55,134
Hydrochloric Acid				726				
Chlorine				14				1
Nitrogen Oxides				4				4
Sodium Hydroxide						810		
Sodium Chloride							1,184	
Total Lbs./Hr.	78,588	46,674	926	126,188	75,812	810	26,311	175,699
SCFM	17,280			28,040				45,525

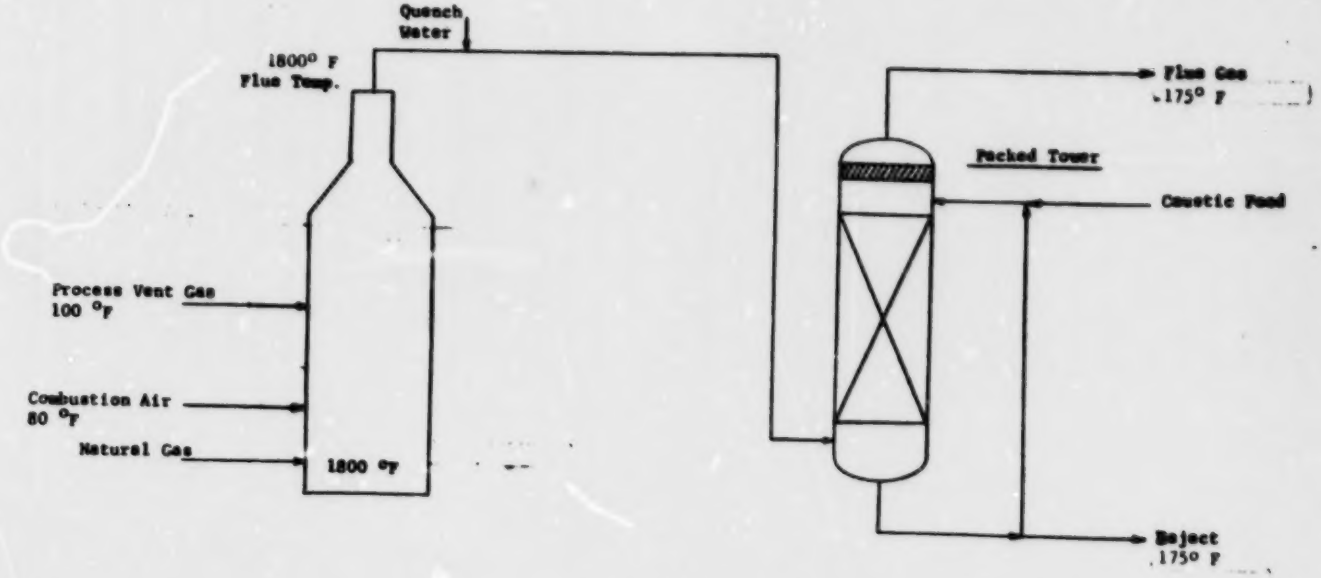
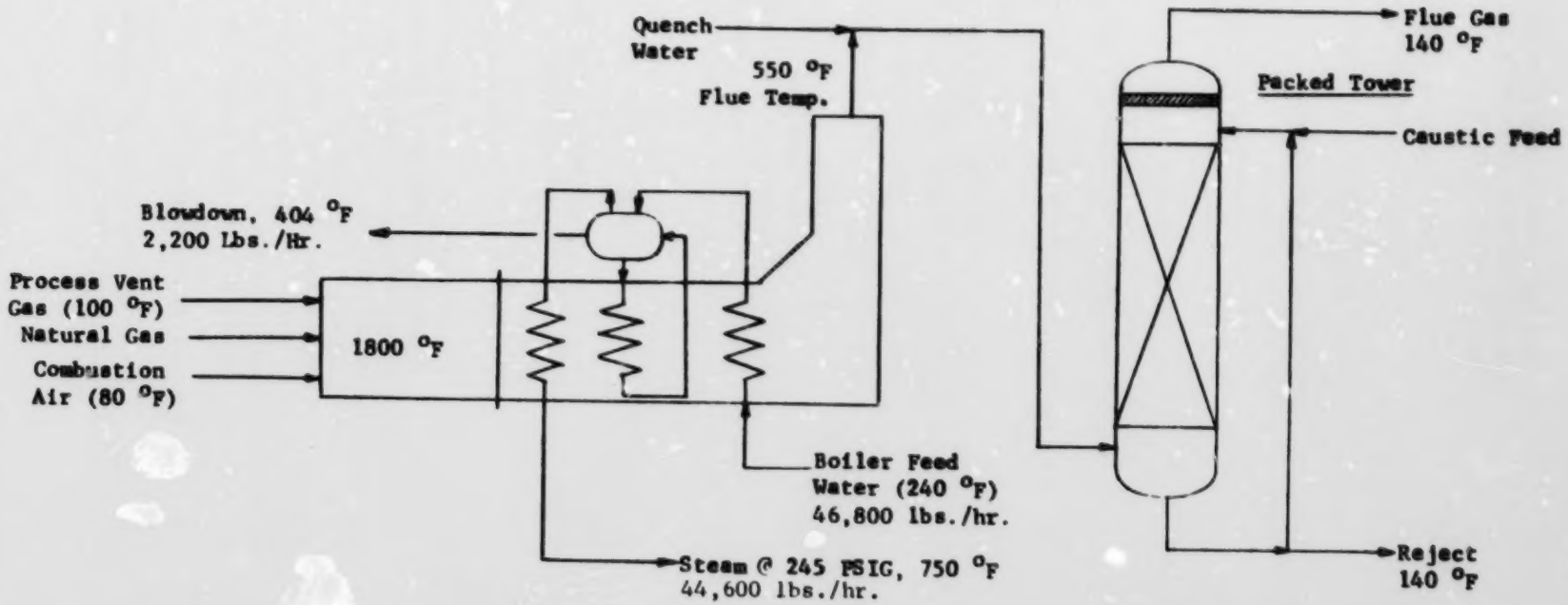


TABLE ED-8
THERMAL INCINERATOR PLUS STEAM GENERATION AND SCRUBBER SYSTEM
FOR
700 MM LB./YR. OXYCHLORINATION PLANT
PROCESS VENT GAS STREAM

MATERIAL BALANCE

Same as shown in Table ED-6

Flow Diagram



therefore, would probably produce somwhat less NOx. However, the application of a catalytic incinerator is not recommended for the following reasons:

(1) Only moderate catalyst life with possible danger of catalyst fouling and poisoning.

(2) Limited oxidation activity.

(3) Based on thermodynamic equilibrium data (8), low operating temperatures would favor increased chlorine production. Chlorine is more difficult to remove than HCl in downstream scrubbing facilities.

(f) Flare System

This control device would have the following limitations:

(1) A substantial amount of supplemental fuel is required to burn this vent stream. Based on recommendations from vendors, about 125 BTU/SCF is the minimum flareable heating value. This would require about 100 MM BTU/hr. of supplemental fuel.

(2) All HCl formed during combustion (about 0.008 T/T EDC) would be emitted to the atmosphere.

(3) Efficiency for removing contaminants is less than for other combustion devices. Based upon qualitative data from similar control devices in other applications, it is estimated that approximately 90 percent of the CO and hydrocarbon pollutants will be burned.

(4) Improper firing of the burner could result in operating temperatures which favor NOx formation.

(5) Changes in vent gas composition could extinguish the burner if adequate instrumentation are not provided.

3. Non-Combustion Devices

As noted in Section II and Section III, A-1, one oxychlorination process incorporated chlorine addition in order to obtain an economically optimum conversion of ethylene. From a conceptual standpoint it should be possible to increase the size of the direct chlorination reaction system in order to reduce ethylene emissions to 10 to 100 PPM rather than the present 2000-8000 PPM level. The process licensor believes that the increased conversion of ethylene to EDC with this modified direct chlorination scheme would off-set the resulting incremental operating costs.

B. Product Fractionation Vent

Four of the surveyed plants (52-1, 52-3, 52-5 and 52-6) have product distillation facilities. The fractionation results in the

atmospheric venting of chlorinated hydrocarbons, which are primarily emitted from the product drying column or "heads" colums. Two of the plants (52-3 and 52-5) have pollution control devices on this stream. In these units, emissions are reduced by cooling the tower off-gas to 55-60° F. The cooled effluent is sent to a phase separator where about 85 percent of the contained hydrocarbons are removed and recycled for EDC recovery. Without a control device, the vent stream (80-120° F) would contain about 0.01 tons of hydrocarbon per ton of EDC production.

In addition to the drying or "heads" column vent, three of the plants emit a small amount of hydrocarbon from one of the following miscellaneous operations:

1. Absorber lean oil stripping (52-6).

2. Waste water stripping (52-5).

3. EDC product caustic scrubber (52-3).

Only one of these plants (52-5) has a pollution control device on this small vent stream. The device, which is similar to that used on the primary fractionation vent stream, removes approximately 70 percent of the contained hydrocarbons. Without vent gas cooling, hydrocarbon emissions are about 0.002 T/T of EDC production.

Recovery of EDC from liquid condensed from the various product fractionating vent streams off-sets the cost of providing the emission control facilities.

If a combustion device was used in place of low temperature cooling, hydrocarbon emissions in these vent streams could be eliminated. However, operating costs would be higher (no EDC recovery) and substantial amounts of HCl (0.009 T/T EDC) would be emitted to the atmosphere. If the combustion device were to be employed downstream of the present pollution control facilities, the unrecovered hydrocarbon (0.0022 T/T EDC) would produce less HCl (0.0013 T/T EDC).

C. Product Storage Vent

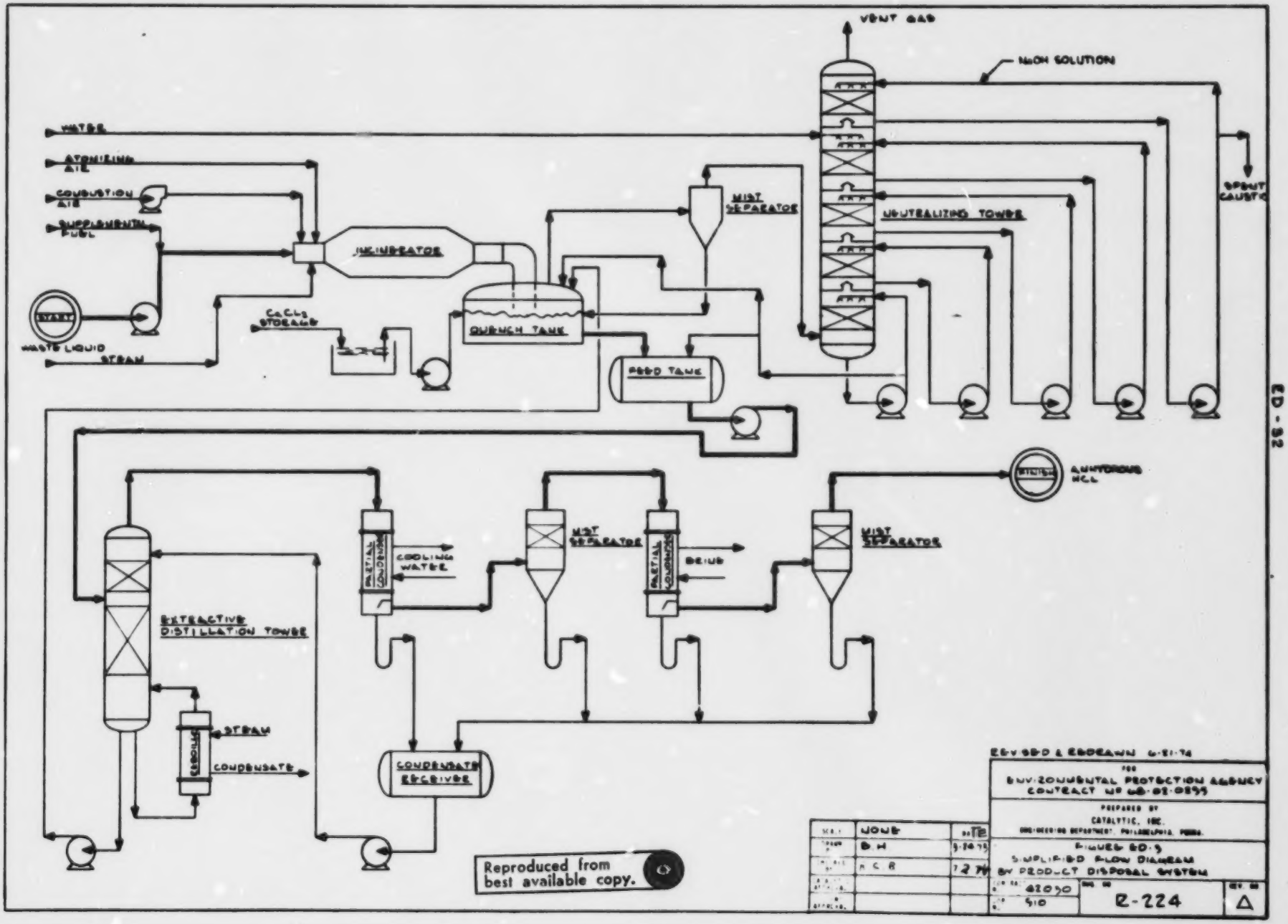
Normally, product storage capacity is equal to about 1.5 to 2 days production. In present plants fixed roof storage tanks are used and these tanks are vented to the atmosphere. Changes in tank liquid level could result in losing as much as 0.06 percent of the EDC product to air emissions. This loss could be eliminated by using floating roof tanks, or vent condensors.

In crude EDC storage, losses are not significant because the product is normally stored under a water layer which effectively reduces EDC vaporization.

D. Waste By-Product Disposal

1. Thermal Incineration

At least one plant (52-5) sends liquid chlorinated hydrocarbons (0.0075 T/T EDC) rejected from the heads column (Table ED-1, Stream 9)



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FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO 68-02-0555

PREPARED BY
CATALYTIC, INC.
ENGINEERING DEPARTMENT, PHILADELPHIA, PENNA.

FIGURE 6D-3
SIMPLIFIED FLOW DIAGRAM
BY PRODUCT DISPOSAL SYSTEM

DRAWN	JOUB	5-20-75
CHECKED	B.H	5-20-75
APPROVED	A.C.B	7-2-75

CAT NO 82030
DWG NO E-224
REV NO Δ

6D-32

to an off-site incinerator for disposal. Effluent from the incinerator is quenched and sent to a three stage absorber for recovery of HCl. Essentially all of the contained HCl is absorbed in dilute hydrochloric acid. The stream is fractionated by azeotropic distillation and dried to yield anhydrous HCl. Unrecovered HCl and the small amount of chlorine formed during incineration are removed by dilute caustic scrubbing before atmospheric venting of the incinerator effluent.

A system similar to that used in plant 52-5 replaces the azeotropic distillation system with a pressure-stripping of dilute HCl (18° BE') followed by successive partial condensations. This represents another method of recovering anhydrous HCl from the incinerator effluent.[14]

Plant 52-10 plans to install an incinerator for burning the main process vent gas plus waste chlorinated by-products. This unit, which will not provide HCl recovery, was expected to be placed on-stream during the last half of 1973. (The current status is unknown.)

A submerged exhaust incinerator followed by an HCl recovery system is another efficient by-product disposal system.[8] Figure ED-3 presents a flow diagram for a typical system that could be used to burn the chlorinated waste and recover anhydrous HCl. In this facility, the liquid chlorinated hydrocarbons are burned in a high performance furnace. A limited amount of excess air (about 15 percent above stoichometric requirement) and high combustion zone temperature are used in order to minimize chlorine formation while obtaining complete combustion. If the hydrocarbon waste contains more than 70 wt. percent chlorine, supplemental fuel is required to obtain adequate temperatures. The hot combustion gases are sparged through a downcomer tube into liquid contained in a quench tank. By direct contact heat exchange, the incinerator effluent is cooled to about 190° F. Concentration of hydrogen chloride in the cooled exhaust gases is usually less than 10 vol. percent since it is diluted with water evaporated from the quench tank. After being quenched, the incinerator effluent is sent to an absorber column. In this multiple bed packed tower, most of the HCl is absorbed in water, producing dilute hydrochloric acid (15 wt. percent HCl). Chlorine and trace quantities of unrecovered HCl are removed from the absorber effluent by caustic scrubbing. The resulting stack gases are reported to contain less than one PPM HCl and ten PPM chlorine.

Since the acid concentration produced in the absorber is less than the azetropic composition (20.2 wt. percent HCl), it is necessary to use extractive distillation in order to obtain anhydrous HCl. Calcium chloride is normally used as the extraction solvent. The azeotrope between HCl and water does not exist when the concentration of calcium chloride reaches 30 percent.

The dilute acid from the absorber is combined with concentrated calcium chloride solution from the incinerator quench tank and charged to a packed bed extractive distillation column. The tower bottoms consists of solvent and water extracted from the dilute acid. This dilute solvent is recycled to the incinerator quench tank for water removal. The overhead HCl vapor from the extractive distillation column is cooled by water condensers and brine coolers to approximately 15° F. The product hydrogen chloride contains 100 PPM chlorine, 60 PPM water and 10 PPM organics.

Overall HCl recovery efficiency is reported to be 95 percent.[8] Future water pollution regulations may favor this or similar types of high recovery systems over systems that employ extensive caustic scrubbing.

2. Catalytic Processing

A commercially proven process is available for converting waste chlorinated hydrocarbons into low cost perchloroethylene and trichloroethylene.[15] This process uses oxygen in fluidized bed reactors to convert the wastes into usable products.

The B.F. Goodrich Chemical Company has claimed the development of a catalytic oxidation process in which chlorinated hydrocarbons are destroyed at relatively low temperatures producing a gaseous product stream which can be fed into the oxychlorination reactors where the contained HCl is converted into EDC. The remaining gases are vented with the oxychlorination unit main process vent stream. The process, which is called CATOXID, is reported to possess the following characteristics:

1. Complete destruction of all types of chlorinated wastes.

2. Low capital investment.

3. Complete recovery of chlorine value as gaseous hydrogen chloride.

4. Low maintenance and minimum operating hazards because of mild operating conditions.

5. Heat recovery in the form of high pressure steam, costly feed pretreatment is not required.

The first commercial CATOXID unit was expected to come on stream in the first quarter of 1974. Its current status is unknown.

E. Best Emission Control Systems

If it is deemed adequate to only reduce unsaturated hydrocarbon emissions, it should be possible to accomplish this by including direct chlorination facilities downstream of the main oxychlorination reactors. The solution, however, porbably does not meet the requirements for a "best" or "most feasible" emission control system.

The most feasible method of reducing total air emission from existing oxychlorination plants would be to provide a thermal incinerator and scrubber on the main process vent stream (Table ED-7) and a plume burner on the product fractionation vent. Before burning the product distillation vent gases, these streams should be cooled to 55-60° F in order to recover EDC and other chlorinated compounds.

Conceptually, the best pollution control system for reducing total air emissions in new units would include a thermal incinerator, waste heat boiler and final caustic scrubber on the main process vent stream, see Table ED-8. After EDC recovery, the product fractionation vent streams should also be sent to this incinerator. However, as previously noted, there is insufficient commercial experience available to determine if this control technique is practical.

If liquid chlorinated by-products are to be burned, the effluent should be sent to an efficient HCl removal system or used to produce desirable chlorinated hydrocarbons.

In future oxychlorination plants that use tonnage oxygen, all hydrocarbon vent streams from the EDC plant could be sent to the same incinerator and HCl recovery system.

Floating roof storage tanks in all new plants would reduce EDC losses from product storage facilities.

F. Industry Research Efforts

Current industry effort in air pollution control centers around development of more selective catalysts which will reduce the amount of chlorinated by-products and increase ethylene conversion. Individual manufacturers are involved in studies regarding the following:

1. Developing markets for chlorinated compounds rejected in product distillation section.

2. Removal of chlorinated hydrocarbons from water reject streams.

3. Recovery of vent material from product storage tanks.

4. Methods of reducing ethylene emissions during catalyst conditioning.

5. Additional direct chlorination stages to reduce ethylene emissions.

V. National Emission Inventory

Based upon the emission factors shown in Table ED-3A, the total approximate emissions from U.S. manufacture of EDC in oxychlorination plants are as follows:

Component	Average Emissions [a] T/T of EDC	Total Emissions [b] MM lbs./yr.
Hydrocarbons		
Ethylene	0.0055	18.8
Total Other Non-Methane Hydrocarbons [c]	0.0224	76.3
Particulates & Aerosols [d]	0.0001	0.4
CO	0.0064	21.8
	0.0344	117.3

The above figures do not include any emissions resulting from off-site processing of waste water and reject hydrocarbon streams. It should be noted that about 55 percent of the oxychlorination EDC production is in plants that did not show product fractionation facilities in the survey reports, see Table ED-3A. Since all of these particular plants also produce vinyl chloride monomer, it is assumed that any undesirable impurities in the EDC are rejected in the downstream VCM facilities. In oxychlorination plants that purify EDC (98.5-99 wt. percent product purity), the hydrocarbon emissions resulting from product fractionation equal about 0.005 T/T EDC. If this typical figure is used to project losses for plants which did not show purification facilities, hydrocarbon emissions would be 9.4 million pounds per year higher than value shown.

Ethylene dichloride production rate is fairly constant throughout the year. However, several plants did report slightly lower production during the first quarter of the year. In addition, since cooling water and product storage temperatures are higher in the summer, it is expected that emissions would be slightly above average during the warmer months.

(a) Weighted average based on individual plant emission factors and EDC production figures.
(b) Based on 1,705,000 tons/yr. total EDC production by the oxychlorination process.
(c) Includes 0.0006 T/T of EDC assumed to be emitted from product storage tanks.
(d) Aerosols include HCl and carbon tetrachloride.

VI. Ground Level Air Quality Determination

Table ED-3A presents a summary of air emissions data for the various oxychlorination plants. This table includes emissions from the main process and product fractionation vent streams. Information regarding vapor losses from product storage have not been included but are estimated to be low (about 0.0006 T/T EDC) for the following reasons:

(a) Crude EDC is stored under a water layer to reduce EDC vaporization.

(b) Vapor pressure of EDC is relatively low (2 - 4 PSI) at normal storage tank operating temperatures.

(c) Crude and product EDC storage tanks usually contain conservation type vents with vacuum breakers in order to minimize losses.

Table ED-3A provides operating conditions and physical dimensions of the various vent stacks. The EPA will use this information together with the air emission data to calculate ground level concentrations for latter reporting.

VII. Cost Effectiveness of Controls

Table ED-9 presents a cost analysis for alternate methods of reducing air pollution from the various vents. Economic data presented are for a new plant producing 700 MM lbs./year of EDC and are based on the following:

A. Investment

Purchased cost of boilers was obtained from current vendor quotes for similar packaged type units. Published data [13], were used as an aid in determining incinerator costs. Investment data provided in various plant surveys were employed to estimate installed costs for vent gas coolers and scrubbers. Flare system and plume burner costs for the main process vent were obtained in a special study that was part of the overall contract. For the distillation vent, these costs were derived from questionnaire data for application of similar devices in other processes.

Installation costs for the various packaged units are estimated values based on previous experience in plant construction. A major portion of this costs represents construction labor.

B. Operating Expense

1. Depreciation - 10 year straight line.

2. Interest - Six percent on total capital.

3. Maintenance - Set at 10 percent of investment for boilers and five percent for incinerators. Maintenance costs for most other control devices are based on data provided in plant surveys.

4. Labor - One man per shift used for direct fired boilers and six hours per day for waste heat boilers and incinerators. Virtually no operating labor is required for other pollution control devices.

5. Utilities - Unit costs are based on current typical values for the Gulf Coast area. After existing contracts expire, it is possible that fuel gas cost will rise considerably above figure used in this economic comparison.

   It is assumed that process vent gas streams are available at sufficient pressure to meet ΔP requirements of the various pollution control devices (10-20 inches of water).

In the case involving direct fired boilers, investment costs are based on including a 100 percent spare boiler in order to provide a more dependable steam supply. Since steam coils in the boiler are within the combustion chamber, it is very likely that more operational problems will be experienced with this type of unit than with a waste heat boiler system. This lower reliability may justify providing spare equipment.

Table ED-9 indicates that employing direct fired boilers with downstream scrubbing facilities is not economical even if a stand-by boiler system is not required. Caustic required for effluent neutralization represents a major cost

TABLE ED-9
COST EFFECTIVENESS FOR ALTERNATE EMISSION CONTROL DEVICES
(BASED ON 700 MM LBS./YR. ETHYLENE DICHLORIDE PRODUCTION BY OXYCHLORINATION)

Stream	Main Process Vent Gas								
Type of Emission Control Device	Water Scrubber	Contact Condenser[a]	Direct Chlorination Facilities	Direct Fired Boiler & Caustic Scrubber		Thermal Incinerator & Caustic Scrubber			
Number of Units	1	1	1	2	1	1		1	
Capacity of each Unit, %	100	100	100	100	100	100		100	
Feed Gas									
Total Flow, Lbs./Hr.	78,653	78,494	78,588		78,588			78,588	
SCFM	17,285	17,275	17,280		17,280			17,280	
Composition, Ton/Ton EDC									
Hydrocarbons									
Ethylene	0.0049	0.0049	0.0049		0.0049			0.0049	
Other Non-Methane Hydrocarbons	0.0208	0.0197	0.0197		0.0208			0.0208	
Particulates & Aerosols	0.0007								
NOx									
SOx									
Carbon Monoxide	0.0068	0.0068	0.0068		0.0068			0.0068	
Gaseous Effluent									
Total Flow, Lbs./Hr.	78,588	77,773	78,176		137,040			175,699	
SCFM	17,280	17,220	17,185		31,980			45,525	
Composition, Tons/Ton EDC									
Hydrocarbons									
Ethylene	0.0049	0.0049	0.0001						
Other Non-Methane Hydrocarbons	0.0208	0.0113	0.0197						
Particulates & Aerosols									
NOx					0.0001			0.0001	
SOx									
Carbon Monoxide	0.0068	0.0068	0.0068						
Emissions Control Efficiency [b]									
CCR					100			100	
SERR	2	34	19		100			100	
SE	100 (HCl)	65 (HCl)	98 (C_2H_4)						
Investment, $									
Purchased Cost	125,000	150,000		440,000	165,000	100,000		200,000	
Installation	175,000	200,000		660,000	235,000	150,000		300,000	
Total Capital	300,000	350,000	200,000	1,100,000 [b]	400,000	250,000 [c]		500,000	
Operating Cost, $/Yr.									
Depreciation (10 years)	30,000	35,000		110,000	40,000	25,000		50,000	
Interest on Capital	18,000	21,000		66,000	24,000	15,000		30,000	
Maintenance	12,000	9,000		110,000	16,000	12,500		20,000	
Labor, $4.85/Hr.	6,500	3,000	Operating cost is about equal to value of EDC produced	39,600	6,500	10,000		6,500	
Utilities and Chemicals									
Power, 1¢/KWH	1,500	3,000		10,600	1,600	1,000		2,000	
Fuel, 40¢/MM BTU[f]				59,500		59,500			
Steam, 65¢/MM BTU (200 PSIG, Sat.)		5,600							
Cooling Water, 2¢/M Gal.		5,700							
Process Water, 10¢/M Gal.	1,500				3,700			7,300	
Boiler Feed Water, 30¢/M Gal.				13,700					
Absorption Fluid, 35¢/Gal.		5,000							
Caustic, 4.0¢/Lb.					264,400			266,400	
Total Utilities and Chemicals	3,000	19,300		83,800	269,700	60,500		273,700	
Total Operating Cost	69,500	87,300 [d]		409,400	356,200	123,000		380,200	
Steam Production, 60¢/M Lbs. (250 PSIG Sat.)				(218,400)					
Recovered EDC, 2.5¢/Lb. of EDC		(87,000)							
Net Annual Cost, $/Yr.	69,500	300	0	191,000	356,200	123,000		380,200	
				547,200		503,100			

TABLE ED-9
COST EFFECTIVENESS FOR ALTERNATE
EMISSION CONTROL DEVICES
(BASED ON 700 MM LBS./YR. ETHYLENE DICHLORIDE PRODUCTION BY OXYCHLORINATION)

Stream	Main Process Vent Gas				Product Fractionation Vent	
Type of Emission Control Device	Thermal Incinerator & Waste Heat Boiler & Caustic Scrubber			Flare System (i)	Condenser + Separator	Flame Burner (e,i)
Number of Units	1	1	1	1	1	1
Capacity of each Unit, %	100	100	100	100	100	100
Feed Gas						
Total Flow, Lbs./Hr.		78,588		17,588 (g)	1170	260
SCFM		17,280		17,280 (g)	115	35
Composition, Tons/Ton EDC						
Hydrocarbons						
Ethylene		0.0049		0.0049	0.0001	0.0001
Other Non-Methane Hydrocarbons		0.0208		0.0208 (g)	0.0117	0.0023
Particulates & Aerosols					0.0003	
NOx						
SOx						
Carbon Monoxide		0.0068		0.0068		
Gaseous Effluent						
Total Flow, Lbs./Hr.		137,040			260	>400
SCFM		31,980		>40,000	35	
Composition, Tons/Ton EDC						
Hydrocarbons						
Ethylene				0.0005	0.0001	
Other Non-Methane Hydrocarbons				0.0932	0.0023	0.0002
Particulates & Aerosols (Incl. HCl & CCl_4)				0.0078		0.0012
NOx		0.0001		0.0001		0.0001
SOx						
Carbon Monoxide				0.0007		
Emissions Control Efficiency (h)						
CCE		100		90 (g)		90
SERE		100		62	80	54
SE					83 (BCL)	
Investment, $						
Purchased Cost	100,000	150,000	165,000	66,000	15,000	
Installation	150,000	225,000	235,000	66,000	35,000	
Total Capital	250,000 (c)	375,000	400,000	132,000	50,000	35,000
Operating Cost, $/Yr.						
Depreciation (10 years)	25,000	27,500	40,000	13,200	5,000	3,500
Interest on Capital (6%)	15,000	22,500	24,000	7,900	3,000	2,100
Maintenance	12,500	37,500	16,000	6,600	3,000	1,800
Labor, $4.85/Hr.	10,000	10,000	6,500	1,000	3,000	1,000
Utilities and Chemicals						
Power, 1¢/KWH	1,000	9,600	1,600		2,000	
Fuel, 40¢/MM BTU (f)	59,500			359,000		1,200
Steam, 65¢/MM BTU (200 PSIG, Sat.)						
Cooling Water, 2¢/M Gal.						
Process Water, 10¢/M Gal.			3,700			
Boiler Feed Water, 30¢/M Gal.		13,700				
Absorption Fluid, 35¢/Gal.						
Caustic, 4.0¢/lb.			264,400			
Total Utilities and Chemicals	60,500	23,300	269,700	359,000	2,000	1,200
Total Operating Cost	123,000	130,800	356,200	386,700	16,000 (d)	9,600
Steam Production, 60¢/M Lbs. (250 PSIG Sat.)		(218,400)			(73,400)	
Recovered EDC, 2.5¢/Lb. of EDC					(57,400) (d)	
Net Annual Cost, $/Yr.	123,000	(87,600)	356,200	386,700	(47,800)	9,600
		391,600				

TABLE ED-9
COST EFFECTIVENESS FOR ALTERNATE
EMISSION CONTROL DEVICES
(BASED ON 700 MM LBS./YR.
ETHYLENE DICHLORIDE PRODUCTION BY OXYCHLORINATION) Sheet 3 of 3

FOOTNOTES:

(a) Feed excludes aromatic solvent absorption oil.

(b) Based on vendor quote for similar unit.

(c) Afterburner systems study by Shell Development Company for EPA, (Contract EHS-D-71-3).

(d) Excludes cost for disposal of recovered liquid by-products.

(e) Downstream of condenser recovery system.

(f) It is possible that future fuel cost will be considerably higherthan figure used in this comparison.

(g) Excludes 1,750 SCFM of supplemental fuel.

(h) $$CCR = \frac{\text{pounds of oxygen that react with pollutants in stream to the device}}{\text{pounds of oxygen that theoretically could react with these pollutants}} \times 100$$

$$SERR = \frac{\text{weighted pollutants in - weighted pollutants out}}{\text{weighted pollutants in}} \times 100$$

$$SE = \frac{\text{specific pollutant in - specific pollutant out}}{\text{specific pollutant in}} \times 100$$

See Appendix for details.

(i) By definition, a flare system requires supplemental fuel to support combustion and a plume burner has a self supporting flame.

item in this control system. If dilute acid (2-3 wt. percent HCl) can be utilizied in other process areas, net annual cost could be reduced by 50 percent. Lime slurry, which is less expensive neutralizing agent, could also be used. However, this material would require larger scrubbing equipment and also results in more operating and liquid waste disposal problems then experienced with caustic neutralization.

A thermal incinerator followed by a waste heat boiler and scrubber is projected to be somewhat more economical to operate than using a single direct fired unit ($390,000 vs $402,600). Vent gas emissions from this facility would be similar to the low values predicted for the direct fired boiler. In both cases, supplemental fuel was assumed to be used in place of feed because of corrosion problems resulting from high metal temperatures in the preheat exchanger.

Thermal incineration plus scurbbing of the main process vent gas (without steam generation) has higher operating cost than the above thermal incinerator system. However, this or the much less efficient plume burner could be incorporated in existing plants where steam can not be exported to other process areas.

If primary interest is to remove unsaturates from the main process vent stream, this can probably be accomplished by using direct chlorination. The oxychlorination process licensor that currently incorporates chlorine addition estimates the investment cost for the proposed ethylene clean-up facility would be approximately $200,000 and EDC produced from the recovered ethylene would off-set operating costs. It should be noted that the process licensor has done some research work in this area but further R & D effort is required before this technology can be applied in a commercial unit.

It should be noted that economic data presented for the various combustion facilities are based on processing a typical process vent gas having a heating value of 38 BTU/SCF. If for a particular feedstock, air to hydrocarbon feed ratio, and catalyst (high selectivity), the vent gas heating value is lower, it would be necessary to increase supplemental fuel usage. For example, if the heating value of the vent gas is 30 BTU/SCF and the same amount of gas is processed, supplemental fuel requirements for the thermal oxidizers would be 45 percent higher than the amount used in the "typical" cases. (26 versus 18 MM BTU/hour) For higher heating value gases, less fuel would be required.

Data shown for incinerator system include costs for downstream caustic scrubbing facilities. This neutralizer would replace water scrubbers presently included in several of the oxychlorination processes.

Table ED-9 includes economics for condensing chlorinated hydrocarbons from the product fractionation vent stream and flaring the unrecovered material. In the most feasible new plant, the cooled fractionation vent stream would be sent to the main process vent gas incinerator system. In this case, investment costs and steam production would be similar to those values shown in Table ED-9 for the process vent gas processing. Caustic consumption for effluent scrubbing would increase about 15 percent.

It is estimated that cost for installing the various pollution control equipment in existing plants would be about the same or only slightly higher than for new plant installations shown in Table ED-9. The actual cost differential would largely depend on space availability and location in relation to associated process equipment.

VIII. Source Testing

It is recommended that source sampling should be performed on the feed and effluent streams of the new incinerator being installed by plant 52-10. This represents the only unit where the main process vent stream is burned. It should be noted that vent gas from plant 52-10 is not typical in composition to that emitted by other existing oxychlorination units. However, test data on this plant would be of use in evaluating emissions from future plants which incorporate pure oxygen feed.

It may be desirable to source test around the vent gas scrubber in plant 52-7 or 52-8. Besides determining scrubber efficiency, these tests could be used to confirm the low emissions reported for the chlorine addition process.

IX. Industry Growth Projection

The U. S. annual ethylene dichloride production is estimated to increase to 20.6 billion pounds by 1985, see Figure ED-4. This represents a 12.5 billion pound per year increase over the present production level. It is anticipated that about 40 % of this incremental production will be by the oxychlorination process. This increase will require the construction of approximately 8 new plants between 1972 and 1985, based on an average oxychlorination plant capacity of 700 million pounds per year of EDC.

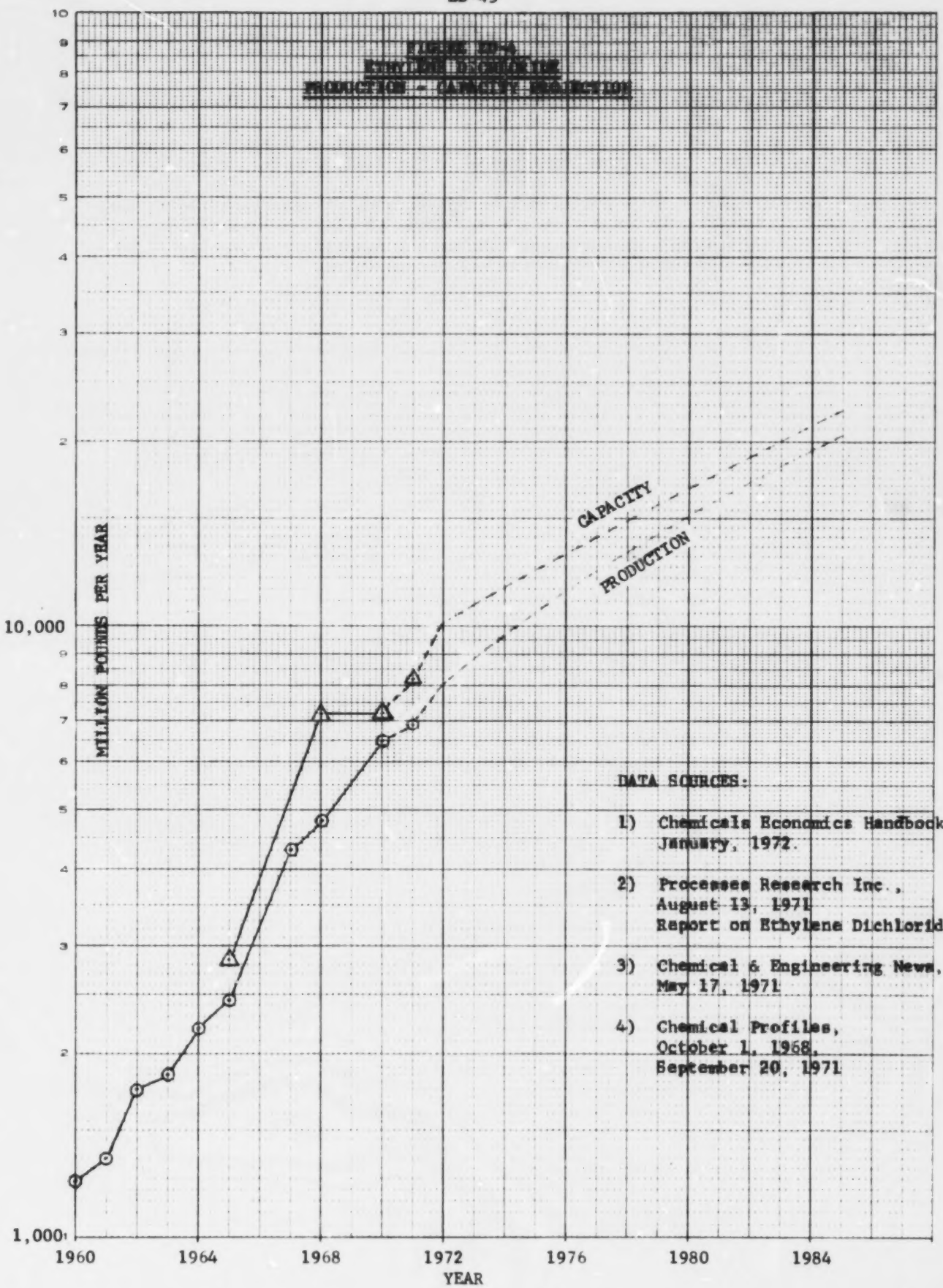
Approximately 80% of all ethylene dichloride produced is used in the production of vinyl chloride monomer (VCM). The previous high growth rate in EDC production (up to 25%/yr.) partly resulted from replacing the older VCM manufacturing process, which used acetylene and hydrogen chloride feed, with the newer ethylene dichloride cracking process. At present over 90% of the U. S. vinyl chloride monomer production is from EDC. Therefore, rather than based on plant conversion, future EDC growth will be more restricted to the actual growth of VCM demand, which is projected to be 8 - 10% per year.

Several new processes are available for VCM production. One process offered by the Lummus Co. [9] produces VCM from ethane and chlorine. This air oxidation process "Transcat" is reported to have a 1¢/lb. lower VCM manufacturing cost primarily because of the use of ethane in place of ethylene feedstock. The Chloe process [10] (Produits Chimique Pechiney - Saint-Gobain, France) produces VCM from ethylene, chlorine and recycle chloroethanes, which permits a wide variation in the net VCM and other chlorinated compounds produced. If either of these processes are used for a significant portion of future VCM production, EDC demand will be reduced.

About 8% of the EDC produced in the U. S. is used as chlorinated-solvent intermediate. While market demand for one of these solvents, trichloroethylene, could possibly decline for ecological reasons, the overall demand in this area is expected to increase 7 - 8% per year.

Approximately 5% of the EDC is used to produce ethyleneamines and 3% is employed as a lead scavenger in gasoline antiknock fluids. Whereas the growth in amine production is expected to grow 7% per year, the gasoline additive demand will decrease during the next few years as lead-free gasoline comes into general use.

In 1971 about 5% of U. S. ethylene dichloride was exported. However, as more foreign plants are built, these exports are expected to decline.


MILLION POUNDS PER YEAR
10,000
1,000
1960
1964
1968
1972
1976
1980
1984
YEAR
CAPACITY
PRODUCTION
DATA SOURCES:
1) Chemicals Economics Handbook, January, 1972.
2) Processes Research Inc., August 13, 1971 Report on Ethylene Dichloride
3) Chemical & Engineering News, May 17, 1971
4) Chemical Profiles, October 1, 1968, September 20, 1971

X. Plant Inspection Procedures

Plant inspections will be conducted by the appropriate authorities, either on a routine basis or in response to a complaint. A quick inspection of plant operations will often suggest whether or not a plant is exceeding allowable emission limits. Among the items which can be easily checked are:

A. High levels of impurities in feed streams. A major portion of many impurities may appear as air emissions if the vent gas is not incinerated. However, most of these impurities are usually light saturated hydrocarbons which are non-reactive.

B. Excessive vent gas flow rate.

C. Visual appearance of plumes of incinerator and other stack gas streams.

D. Discernible odor of HCl or chlorine within the plant.

If the inspector has reason to suspect that emissions are excessive, some factors that he should consider and/or discuss with plant officials are itemized below:

A. Process Vent Gas scrubbers

Proper operation of the water and caustic scrubbers are necessary to limit emissions of HCl and chlorine from the process vent stream. This vent stream should be essentially odorless and colorless. If the scrubber is downstream of an incinerator, the effluent should have the appearance of steam with no residual plume. Excessive vent gas emissions could be caused by:

1. Liquid and feed gas flow rates above design values.

2. Temperature and pressure of vent gas plus process side pressure drop across the tower being different than normal plant operating and design values.

3. Improper waste water pH control. This can result in inefficient removal of HCl and chlorine. Normally a pH of 7-8 is adequate to remove HCl. A higher value may be necessary for complete removal of chlorine.

4. Feed gas temperature exceeding design value. This could result in excessive carryover of hydrocarbons. High temperatures could result from inadequate cooling of the oxychlorination reactor effluent.

B. Process Vent Gas Absorber and Contact Condensers

Proper operation of this equipment is necessary in order to limit hydrocarbon emissions. Vent gas from plants that incorporate this recovery equipment should be odorless and colorless. If malfunctioning of equipment is suspected, it could be caused by:

1. Abnormal feed gas and circulating liquid flow rates.

2. Temperature and pressure of vent gas and process side pressure drop being different than normal plant operating and design values.

3. High operating temperature resulting from (a) inadequate cooling of the oxychlorination reactor effluent (b) excessive feed or (c) inadequate cooling within the recovery system, would increase hydrocarbon losses.

C. Product Fractionation Vents

Temperature of vent streams should not exceed design values. High temperatures could result from insufficient cooling (refrigeration) or excessive flow rate. High flow could be caused by maloperation of the fractionators, poor selectivity in the oxychlorination reactors or the plant production exceeding design EDC production capacity.

D. Incinerators

Proper operation of by-product and vent gas incinerators (if present) is necessary to insure low emissions. Since most incinerators are followed by scrubbing towers it is not usually possible to determine incinerator performance by a visual inspection of the scrubbed vent gas. Smoke meter readings on the scrubber feed are desirable in order to see if the furnace is functioning properly. Smoke-free combustion requires adequate time, good turbulence in mixing fuel and air plus sufficient temperature for the reaction to proceed to completion and produce the desired products of oxidation. The following measures are normally recommended by manufacturers as methods to improve performance of a smoky incinerator;

1. Usually smoke results from low combustion zone temperature (below 1400° F) or improper fuel to air ratio. If combustion zone temperature is low it may be desirable to consider reducing the amount of excess air or add supplemental fuel. Variation in overall feed composition could also result in low operating temperatures.

2. If operating temperature appears adequate and the furnace still smokes, it may be necessary to increase air rate to the incinerator in order to insure complete combustion. However, large amounts of excess air normally should be avoided since this favors chlorine formation in the combustion of chlorinated hydrocarbons.

XI. Financial Impact

Table ED-10 presents economics for ethylene dichloride manufacture in a typical 700 MM lbs./year oxychlorination plant that incorporates a minimum of air pollution control equipment (water scrubber on the main process vent gas stream). Based on present cost/price levels, the production of EDC by the oxychlorination process appears to be fairly profitable (ROI = 13.5%)*.

Table ED-11 provides economics for producing EDC in an existing plant modified to reduce emissions. Modifications consist of adding an incinerator plus caustic scrubber on the main process vent stream and condensing chlorinated hydrocarbons from the product fractionation vent prior to burning the resulting non-condensibles in a plume burner.

Table ED-11 also shows estimated economics for producing ethylene dichloride in a new most feasible oxychlorination unit. This plant includes a thermal incinerator for burning the main process vent gas and the net product fractionation vent (after EDC recovery). Incinerator effluent is sent to a waste heat boiler for steam generation and neutralized with caustic in a packed tower. In addition, EDC product is assumed to be stored in floating roof tanks ($30,000 incremental investment for 350,000 gallon tank) in order to reduce hydrocarbon losses.

The economic data indicate about a 0.05¢/lb. increase in EDC production cost for both the modified and new most feasible units. Assuming an EDC selling price of 3.0¢/lb., this corresponds to a 20 to 26 percent reduction in profit and reduces return on investment to about 9.0 percent. Table ED-11 also shows the effect of variations in capital charges and net operating cost of pollution control equipment on ROI. It is conceivable that a small part of the incremental cost for the proposed pollution system in new plants could be off-set by deletion of scrubbing facilities currently used in some oxychlorination processes. It is also possible that costs could be somewhat higher if the value of EDC recovered from the fractionation system vent is less than assumed (2.5¢/lb.).

Table ED-12 presents pro forma balance sheets for the above cases. It was assumed in developing these asset and liability positions that the ethylene dichloride selling price would be held constant and any variation in production costs would be taken out of profit margin in order to maintain sales volume. Capital requirement for the most feasible new plant is about 1.1 million dollars higher than for an existing type plant.

In addition to financial impact, it is essential to evaluate the overall environmental impact of the most feasible method of emission control. A prime factor for consideration in this evaluation is the effect on fuel savings. If the vent gas streams are burned and energy recovered as steam in all future plants, the net energy savings will be equivalent to about 1.6 billion standard cubic feet per year of natural gas by 1985. This could be a direct savings in natural gas or savings in energy output from coal or liquid residual fuels which also represent sources of air pollution. However, if no steam is produced in these units, net fuel consumption will be equivalent to 1.1 billion standard cubic feed per year of natural gas higher than for the same units without pollution control.

*However, it should be noted that the cost of raw materials is the major factor in determining the cost of EDC (over 80 percent of total cost). Conversion cost is relatively low and capital related items are relatively important in this process.

TABLE ED-10
ETHYLENE DICHLORIDE MANUFACTURING COST
FOR A TYPICAL (MODEL PLANT)
EXISTING 700 MM LB./YR. OXYCHLORINATION FACILITY

DIRECT MANUFACTURING COST	¢/LB.	$/YR.
Raw Materials		
99.9% Ethylene @ 3.25¢/lb.	1.06	
Anhydrous HCl @ 1.75¢/lb.	1.19	
Catalyst and Chemicals	0.04	
Labor (3 men/shift @ $4.85/Hr.)	0.02	
Maintenance (5% of Investment)	0.04	
Utilities	0.06	
	2.41	
INDIRECT MANUFACTURING COST		
Plant Overhead (110% of Labor)	0.02	
FIXED MANUFACTURING COST		
Depreciation (10 Years)	0.09	
Insurance & Property Taxes (2.3% of Inv.)	0.02	
	0.11	
MANUFACTURING COST	2.54	
GENERAL EXPENSES		
Administration (3% of Manufacturing Cost)	0.08	
Sales (1% of Manufacturing Cost)	0.03	
Research (2% of Manufacturing Cost)	0.05	
Finance (6% of Investment)	0.05	
	0.21	
TOTAL COST	2.75	19,250,000
Selling Price	3.00	21,000,000
Profit Before Taxes	0.25	1,750,000
Profit After 52% Tax	0.12	840,000
Cash Flow		1,460,000
ROI (NPAT x 100/Plant Investment)		13.5%

TABLE ED-11
ETHYLENE DICHLORIDE MANUFACTURING COST
FOR A TYPICAL MOST FEASIBLE
700 MM LBS./YR. OXYCHLORINATION FACILITY

Type of Unit	Modified Existing Plant (b)		New Plant (b)	
DIRECT MANUFACTURING COST	¢/LB.	$/YR.	¢/LB.	$/YR.
Raw Materials				
99.9% Ethylene @ 3.25¢/lb.	1.06		1.06	
Anhydrous HCl @ 1.75¢/lb.	1.18		1.18	
Catalyst and Chemicals	0.08		0.08	
Labor	0.02		0.02	
Maintenance	0.05		0.05	
Net Utilities	0.07		0.04 (a)	
	2.46		2.43	
INDIRECT MANUFACTURING COST				
Plant Overhead (110% ob Labor)	0.02		0.03	
FIXED MANUFACTURING COST				
Depreciation (10 Years)	0.10		0.10	
Ins. & Prop. Taxes (2.3% of Inv.)	0.02		0.02	
	0.12		0.12	
MANUFACTURING COST	2.60		2.58	
GENERAL EXPENSES				
Administration (3% of Mfg. Cost)	0.08		0.08	
Sales (1% of Mfg. Cost)	0.03		0.03	
Research (2% of Mfg. Cost)	0.05		0.05	
Finance (6% of Investment)	0.06		0.06	
	0.22		0.22	
TOTAL COST	2.82	19,710,000	2.80	19,600,000
Selling Price	3.00	21,000,000	3.00	21,000,000
Profit before Taxes	0.18	1,290,000	0.20	1,400,000
Profit after 52% Tax	0.09	619,000	0.10	672,000
Cash Flow		1,322,000		1,406,000
ROI (NPAT x 100/Plant Investment)	8.8%		9.2%	
ROI Sensitivity				
Increased Capital Charges (c)	6.8%		6.5%	
Increased Operating Cost (d)	5.1%		5.9%	

(a) Assumes 0.031¢/lb. credit for steam produced in pollution control waste heat boiler.
(b) Economics for pollution control equipment obtained from Table ED-9.
(c) Capital charges for pollution control equipment double values shown in Table ED-9.
(d) Capital charges and net operating cost for pollution control equipment double values shown in Table ED-9.

TABLE ED-12
PROFORMA BALANCE SHEET
700 MM LB./YR. OXYCHLORINATION FACILITY

Type of Unit	Existing	Modified Existing	Most Feasible New
Current Assets			
Cash (A)	$ 1,481,700	$ 1,516,700	$ 1,505,000
Accounts Receivable (B)	1,750,000	1,750,000	1,750,000
Inventories (C)	1,925,000	1,974,000	1,960,000
Fixed Assets			
Plant	6,200,000	7,035,000	7,340,000
Building	100,000	100,000	100,000
Land	50,000	50,000	50,000
Total Assets	$11,506,700	$12,425,700	$12,705,000
Current Liabilities (D)	$ 1,510,800	$ 1,540,000	$ 1,528,000
Equity & Long Term Debt	9,995,900	10,885,700	11,177,000
Total Capital	$11.506,700	$12,425,700	$12,705,000

(A) Based on one month's total manufacturing cost.
(B) Based on one month's sales.
(C) Based on 70 MM lbs. of product valued at total cost.
(D) Based on one month's total cost less fixed manufacturing and finance costs.

XII. Cost to Industry

In the typical plant depicted in Table ED-10, about five percent of the plant investment is directly attributed to cost of air pollution control equipment. This expenditure plus associated operating costs equals less than 0.5 percent of the EDC total production cost (0.01¢/lb.). If the cost of raw materials is deducted, the air pollution control contributes about three percent of the conversion cost.

Total capital cost for modifying all existing plants to incorporate incineration and scrubbing facilities on the main process vent stream and condensers plus plume burners on the fractionation vent streams would be about $5,000,000. In the "most feasible new plant" presented in Table ED-11, air pollution control equipment represents about 15 percent of the total plant investment. Assuming all new oxychlorination plants built between now and 1985 incorporate this type of air emission control equipment, the total incremental capital cost for these plants will be about $9,000,000.

The 0.05¢/lb. higher EDC production cost indicated in Table ED-11 for modified and new plants should not reduce growth in demand for ethylene dichloride by the oxychlorination process. However, this increase plus an increase in raw materials costs could reduce the industry growth and result in the use of substitute materials.

The projected effect of the above expenditures on future air emissions is shown in Table ED-13.

TABLE ED-13
ESTIMATED 1985 AIR EMISSIONS FOR ALTERNATE CONTROL SYSTEMS

Type of Pollution Control	Present System			Most Feasible Modifications								
				Existing Plants (D)			New Plants (E)			Total (D,E)		
EDC Production, (A) Tons/Yr.	4,205,000			1,705,000			2,500,000			4,205,000		
Pollutant (B)	Average Emissions T/T	Total Emissions MM Lbs./Yr.	Weighted Emissions	Average Emissions T/T	Total Emissions MM Lbs./Yr.	Weighted Emissions	Average Emissions T/T	Total Emissions MM Lbs./Yr.	Weighted Emissions	Average Emissions T/T	Total Emissions MM Lbs./Yr.	Weighted Emissions
Hydrocarbons:												
Ethylene	0.0055	46.3	3,700									
Other Non-Methane Hydrocarbons	0.0224 (G)	188.4	15,070	0.0007 (G)	2.4	190				0.0003	2.4	190
Particulates & Aerosols (C)	0.0001	0.8	50	0.0009	2.9	175				0.0004	2.9	175
NOx				0.0001	0.4	15	0.0001	0.6	25	0.0001	1.0	40
CO	0.0064	53.8	50									
	0.0344	289.3	18,870 (F)	0.0017	5.7	380 (F)	0.0001	0.6	25	0.0008	6.3	405 (F)

(A) Estimated production by oxychlorination process.

(B) Excludes emissions resulting from off-site product fractionation and by-product disposal.

(C) Includes HCl and carbon tetrachloride.

(D) Assumes all existing plants modified to incorporated thermal incinerators and scrubbers on process vent stream plus distillation vent condensers and plume burners.

(E) New plants assumed to contain floating roof product storage tanks and based on thermal incineration on process and distillation vent streams with waste heat boiler and caustic scrubber with distillation vent condenser before incineration.

(F) Significant Emission Index, which is based on the following weighting factors: Hydrocarbon = 80, Particulates = 60, NOx = 40, and CO = 1. (See Appendix)

(G) Includes 0.0006 T/T of EDC lost from product storage tanks in existing units.

XIII. Emission Control Deficiencies

Technical deficiencies which hinder reducing the level of emissions include the following:

A. Process Chemistry and Kinetics

In the oxychlorination process, a cupric chloride catalyst is used to produce EDC. Based upon experimental data it is believed that the reaction proceeds by formation of an ethylene-oxygen complex, which is subsequently chlorinated to ethylene dichloride by either HCl or cupric chloride. The rate determining step is the ethylene oxidation reaction.

The amount of ethylene dichloride produced is influenced by the relative concentration of feed components, reactor residence time and other operating conditions.

1. Reactor Feed

(a) Ethylene

Unsaturated hydrocarbon impurities in the ethylene feed can react with HCl forming undesirable chlorinated by-products. Therefore, in order to minimize air pollution and maximize productivity it is desirable to use high purity ethylene. In all but one plant, ethylene feed contains less than one percent impurities. In the one case (52-1) where low purity feed (82-92 percent ethylene) is utilized, chlorinated and non-chlorinated hydrocarbon emissions are substantially higher than with the conventional feed. In some cases economics dictate using some excess ethylene to insure high HCl conversion. This excess olefin is normally vented to the atmosphere, but could probably be recovered by a direct chlorination step.

(b) Oxygen Concentration

All but one oxychlorination unit uses air as a source of oxygen. By utilizing pure oxygen in place of air, plant 52-10 has been able to reduce the volume of vent gas. Even though the total quantity of hydrocarbon emissions are similar to those for the other units, most of this material consists of unconverted ethylene. Besides containing less chlorinated material, it should be less difficult and cheaper to control the quantity of emissions from this source.

(c) Hydrogen Chloride

Again, depending upon economics, some excess HCl may be fed to the reactors to insure high ethylene conversion. One published article [11] indicates that excess HCl leads to the formation of unwanted chlorinated by-products.

2. Reactor Operating Conditions

Reactor operating conditions influence ethylene conversion rate and to a certain extent the amount of non-selective products. Since

unconverted ethylene is lost in the process vent gas stream, operating conditions are adjusted to obtain high ethylene conversion and maximum EDC projection.

3. Catalyst

With the catalysts presently employed, ethylene to EDC selectivity is 90-95 mol percent. Non-selective products contribute to CO and hydrocarbon emissions in the main process vent gas. In addition, light and heavy chlorinated hydrocarbon by-products are formed, which have little or no economic value. Removal and disposal of these compunds can result in air pollution problems.

B. Process Equipment and Operations

1. Reactors

The chemical reaction for EDC production is highly exothermic. For this reason some oxychlorination processes utilize fluid bed reactors with internal cooling coils. This type of reactor results in some catalyst carry over in the effluent stream. However, this catalyst (0.0002 T/T of EDC) is normally completely removed in the effluent scrubbing facilities. In fact only one plant (52-6) mentioned particulate emissions, and in this case they were indicated to be nil. It is conceivable, that during emergencies which cause shut down of the scrubbers, some particulate emissions could occur.

2. Plant Operation

Several plants do not analyze the process vent gas on a frequent basis. Plant 52-6, which normally makes these analyses on a continuous basis, indicates that these data are important in controlling plant operation. A continuous record of ethylene content is desirable to maximize feedstock utilization and limit hydrocarbon emissions.

C. Control Equipment and Operations

1. Scrubbers

Water or dilute caustic is used to remove unreacted effluent prior to venting of non-condensibles. The resulting reject waste water plus water condensed from the reactor effluent contains some dissolved light chlorinated hydrocarbons. Subsequent off-site processing of this reject water can result in hydrocarbon air emissions. In the one oxychlorination plant that has on-site water strippers for recovery of EDC (plant 52-5), hydrocarbon air emissions are about 0.0005 T/T of EDC.

2. Process Vent Gas Emission Control

The proposed incineration and caustic scrubbing of the process vent gas stream is the most feasible method of reducing air emissions from this stream. The deficiencies in this treatment are that is results in production of a small amount of NOx and increases the amount of reject waste water.

3. By-Product Disposal

The proposed incineration and downstream recovery of HCl is the best method of reducing air emissions from product fractionation vent gas and liquid by-product disposal. However, the same type of deficiencies exist as are indicated for the process vent gas control system.

XIV. Research and Development Needs

If the technology deficiencies discussed under Section XIII are to be overcome, additional R & D is desirable in the following areas:

A. Existing Plants

1. Improved Catalyst

It would be desirable to have a more selective catalyst in order to reduce air emissions and produce less unwanted chlorinated by-products. Catalyst development work in this area can best be handled by the process licensors.

B. New Plants

1. Recycle Vent Gas

A combination of pure oxygen feed in place of air and recycle of vent gas to the reactors could reduce net emissions and improve feed utilization. By using a recycle system it may be possible to reduce the amount of excess HCl employed and improve EDC selectivity.[11] With the recycle processing scheme, it probably would be desirable to reduce ethylene conversion rate in order to further improve selectivity.

2. Modified Raw Materials

In order to improve utilization of ethylene and reduce hydrocarbon emissions, it may prove beneficial to substitute chlorine for part of the HCl reactor feed. This proposed R & D study would employ pure oxygen feed and a vent gas recycle system. The EDC would be produced in a fluidized bed reactor with chlorine added to an intermediate reaction zone.

By having the ability to add chlorine to the oxychlorination reactor, it would be easier to maintain a "balanced" operation. In fact, it may be possible to replace the separate direct and oxychlorination units in a balanced plant with a single dual purpose reactor system.

3. HCl Recovery

Reactor effluent condensation and scrubbing operations associated with the process and emission control devices result in several waste water reject streams. These streams could contain significant amounts of HCl (maximum quantity equals about 0.05 T/T EDC). Neutralization of this acid does not completely alleviate the waste water disposal problem. In addition, any loss of HCl results in an increase demand for HCl or chlorine feed to the overall EDC facility. Therefore, from a water pollution standpoint and in order to conserve raw materials, it is desirable to recover this acid. Unfortunately, the oxychlorination process requires the use of anhydrous hydrogen chloride and there is no economical method of obtaining anhydrous acid from the dilute acid waste water streams (2 - 5% HCl).

It is possible to produce 20 wt. % acid from the reject streams by straight distillation. In order to exceed this concentration,

which represents an azeotropic mixture, it is necessary to use extractive distillation or pressure-stripping followed by successive partial condensations.

In search of a more economical method of recovery, a brief study was made of concentrating weak acid by electrodialysis. However, above five to ten percent HCl concentration, the efficiency of this process is said to drop off radically.[12]

While at the present time there appears to be no practical process available for conentrating dilute HCl, future water pollution regulations may create added incentive for R & D effort in this area.

4. Heat Recovery

Since there is limited commercial data available on chlorination waste incineration with heat recovery, it may be desirable to study corrosion rates and other potential operating problems associated with this type of emission control system.

XV. Research and Development Programs

The following proposed programs are for projects within the general R & D areas listed in Section XIV. These programs are limited to those projects which probably have the best chance of success in reducing emissions from future ethylene dichloride manufacture. It has been assumed that the researcher has an existing technological base, and the capability to design EDC plants.

Project A

1. Title - Oxygen Feed plus Vent Gas Recycle for Reduced Emissions

2. Object

To study the feasibility of a modified oxychlorination process using pure oxygen and vent gas recycle to lower gas emissions.

3. Project Cost (see Table ED-14 for cost breakdown)

Capital Expenditures	$100,000
Operating Costs	
Total Manpower	86,700
Services	6,100
Materials	4,000
Contingency	25,000
	$221,800

4. Scope

The primary purpose of this research will be to modify the pure oxygen oxychlorination process by recycling vent gas to the reactor system for improved utilization of ethylene feedstock and reduced production of chlorinated by-products. These process changes will be studied in a small pilot plant reactor coupled to an on-line gas chromatograph. Successful completion of the project could lead to a pilot plant demonstration utilizing the same pilot plant equipment employed in this study.

5. Program

(a) Construction of Test Unit

This part of the project is concerned with the design, fabrication and start-up of a laboratory scale unit employing a small tubular reactor. It is estimated that construction and checkout of the test unit would require four months.

(b) Process Development

The effect of process operating conditions and recycle gas ratio on conversion, EDC selectivity and composition of effluent gases will be studied. A standard copper chloride catalyst will be used for all studies.

(c) Process Engineering

Data from the process development work will be used to design a model for the oxychlorination process. This model would define

TABLE ED-14
DETAILED COSTS
FOR
R & D PROJECT A

PILOT UNIT DESIGN CONSTRUCTION & CHECKOUT		
Design Manpower:	Professional - 6 weeks	5,600
	Technician - 12 weeks	6,200
Major Equipment, Installed		100,000
Contingency		15,000
		126,800
PROCESS DEVELOPMENT		
Operation		
Manpower:	Professional - 12 weeks	11,100
	Technician - 2 men/shift, 3 shifts/day for 12 wks.	51,600
Services:	Analytical - 150 hours	2,200
	Computational	2,400
Materials		4,000
Contingency		8,000
		79,300
ENGINEERING		
Process Design and Economic Evaluation		
Process Engineer - 20 weeks		12,200
Services: Computational		1,500
Contingency		2,000
		15,700

optimum process parameters for maximum conversion and selectivity at lowest emission levels.

6. Timetable

The overall time required for this project including pilot plant construction, unit operations and engineering evaluation is estimated to be 13 months (excludes equipment delivery time).

Project B

1. Title - Reduction of Vent Gas Emissions from Modified Oxychlorination Process by the Use of Chlorine

2. Object

To study the effect on vent gas emissions of substituting molecular chlorine for a portion of the hydrogen chloride used in the modified oxychlorination process studied in Project A.

3. Project Cost (see Table ED-15 for cost breakdown)

Capital Expenditures	$ 30,000*
Operating Costs	
Total Manpower	70,300
Services	6,100
Materials	3,500
Contingency	15,000
Total	$124,900

*Incremental cost for adding reactor to Project A pilot unit.

4. Scope

On a laboratory scale, modify the revised oxychlorination processing scheme studied in Project A by replacing part of the HCl feed with molecular chlorine in order to improve feedstock utilization and reduce production of chlorinated by-products. It is assumed this study will be performed in the Project A pilot unit modified to include an additional reactor in series with the main oxychlorination reactor.

5. Program

(a) Construction of Test Unit

A small tubular reactor will be constructed and added to the Project A pilot unit.

(b) Process Development

The effect of process operating conditions and HCl and chlorine split on conversion, EDC selectivity and composition of effluent gases will be studied. A standard copper chloride catalyst will be used for all studies.

(c) Process Engineering

Same as Project A

TABLE ED-15
DETAILED COSTS
FOR
R & D PROJECT B

PILOT UNIT MODIFICATION & CHECKOUT

Design Manpower:	Professional - 3 weeks	2,800
	Technician - 6 weeks	3,100
Major Equipment, Installed		30,000
Contingency		6,000
		41,900

PROCESS DEVELOPMENT

Operation		
Manpower:	Professional - 10 weeks	9,200
	Technician - 2 men/shift, 3 shifts/day for 10 wks.	43,000
Services:	Analytical - 150 hours	2,200
	Computational	2,400
Material		3,500
Contingency		7,000
		67,300

ENGINEERING

Process Design and Economic Evaluation	
Process Engineer - 20 weeks	12,200
Services: Computational	1,500
Contingency	2,000
	15,700

6. Timetable

The overall time required for this project including pilot plant modification, unit operations and engineering evaluation is estimated to be 10 months.

XVI. Sampling, Monitoring and Analytical Methods for Pollutants in Air Emissions

Information available on the sampling and analysis of gaseous contaminants is contained in Table ED-16. Sample collection methods employed in the various plants involve the use of either bulb type samplers or continuous vacuum withdrawal. No statements were made in the plant surveys regarding the prevention of condensation of vapors in sampling systems but it probably can be assumed that heating is used where appropriate. As might be expected for analysis of organic vapors, the gas chromatograph is the principal analytical instrument. In most cases, inorganic gases are also analyzed on the same equipment using silica gel or molecular sieve columns.

Only one plant (52-3) furnished sufficient detail to allow reproduction of the sampling and analytical procedures. However, considering the nature of the source and contaminants and assuming reasonable care in performance of these analyses, there appears to be no reason why the methods in use are not entirely adequate for emissions characterization. Therefore, no further analytical development work is considered necessary for this industry.

TABLE ED-16
SUMMARY OF SAMPLING AND ANALYTICAL METHODS
FOR POLLUTANTS FROM
PROCESS VENT STREAMS

Plant No.	Compounds Sampled	Methods
52-1	O_2, CO_2, Ethylene	Continuous, on-stream analyzer - type unknown. Gas flow metered continuously.
	Methane, ethane, vinyl chloride, ethyl chloride ethylene chloride, dichloroethane, dichloroethylene, carbon tetrachloride. chloroform	Sample extracted using 2.5 cc syringe 4 - 6 times per year. Gas chromatographic analysis - details unknown.
	Carbon Monoxide	Determined about 6 times per year - method unknown.
52-2	Carbon monoxide, ethane, ethylene CO_2, dichloroethane, N_2, O_2, argon	Stack gas flow metered by orifice. Samples collected in a rubber volleyball bladder (2 l.) or glass syringe. Analysis by Varian thermal conductivity gas chromatograph. Molecular sieve column for O_2, N_2, CO and argon. Porepak S column for organics and CO_2.
52-3	Ethane, ethylene, vinyl chloride, ethyl chloride, carbon tetrachloride, 1,2 - dichloroethane (all streams)	Sample is collected in a 300 ml. glass bomb for analysis using a Perkin-Elmer Model 154-D double column gas chromatograph. Operating parameters are: detector block - 92° C; column oven - 92° C; detector voltage - 8 volts D. C., - carrier gas-helium; carrier gas flow - 60 ml./sec.; and sample size - 2 ml. Column 1 for detection of ethane and ethylene is ⅛" x 4' s.s. containing Davidson grade 08 silica gel in 30/60 mesh size. Column 2 for detection of vinyl chloride, ethyl chloride, carbon tetrachloride and 1.2- dichloroethane, is ⅛" x 12' s.s. containing 30% silicone DC 550 on 60/80 mesh fire brick. Results are recorded on a Honeywell Electronik 19 Recorder and interpreted with the aid of a Hewlett Packard 3370 A Electronic Integrator. Samples are drawn into a 2 ml. sample loop injector using vacuum on the glass bomb.

TABLE ED-16 CONTINUED
SUMMARY OF SAMPLING AND ANALYTICAL METHODS
FOR POLLUTANTS FROM
PROCESS VENT STREAMS

Plant No.	Compounds Sampled	Methods
52-3	O_2, N_2, CO, CO_2, ethane, ethylene	Sample is collected in a 300 ml. glass bomb for analysis using a Beckman GC-1 gas chromatograph and Honeywell Electronik 19 Recorder. Operating parameters are: detection block - 38° C; injection port - 38° C; column oven - 38° C; bridge current - 10 ma; carrier gas - helium at 30 PSI: and attenuation - 5X. Columns are ¼" x 5' silica gel in series with a ¼" x 3' molecular sieve. The molecular sieve is valved for by-pass immediately following the elution of carbon monoxide. One microliter samples are injected using a 3 ul. syringe.
52-4	Ethylene, ethylene dichloride, methane, O_2, CO_2, CO, N_2	Sample pumped to on-stream, triple column Bendix gas chromatograph. Analyses at 13 minute intervals, by procedure believed to be similar to plant 52-6.
52-5	Methane, ethane, ethylene, ethylene dichloride, solvesso, N_2, CO_2, CO, O_2 plus argon, H_2	Flow measured using pilot tube. Analysis by 3 column, on-stream gas chromatograph, believed to be similar to plant 52-6. Checked with laboratory chromatograph once/week and occasionally against a mass spectrometer.
52-6	Ethylene, dichloro-ethane, O_2, CO_2, CO, N_2	Sample obtained from positive pressure stack through stainless steel tubing and mist filer. Analysis at 13 minute intervals using triple column gas chromatography. Column one (1,2-dichloroethane) consists of 3 feet of 1/8 inch tubing packed with 5% Octoil S on 60/80 mesh chromosorb G. Column two (CO_2, ethylene) consists of 15 feet of 1/8 inch tubing containing 50/80 mesh Porepak S. Column three (O_2, N_2, CO) is a 5 foot by 3/16 inch tubing packed with 30/60 mesh, 5 Angstrom molecular sieve.

TABLE ED-16 CONTINUED
SUMMARY OF SAMPLING AND ANALYTICAL METHODS
FOR POLLUTANTS FROM
PROCESS VENT STREAMS

Plant No.	Compounds Sampled	Methods
52-7, 8 & 9	Ethylene, ethylene dichloride, ethyl chloride, O_2, CO, CO_2	Flow rate determined by nitrogen balance. Occasional gas analyses using a Beckman Model GC-2, triple column gas chromatograph. Silicone oil on a packing is used for chlorinated hydrocarbons, a Porepak Q column for hydrocarbons and a third column of unknown nature for oxygen.
	Chlorine (52-7)	Continuous analysis using ultraviolet spectroscopy.
	Chlorine (52-8 & 9)	A gas sample is bubbled through a potassium iodide solution. Free iodine is titrated with sodium thiosulfate.
	Hydrogen chloride	HCl is collected in a water scrubber and the solution is titrated with sodium hydroxide.
52-10	Ethylene, ethane, ethyl chloride, ethylene dichloride vinyl chloride, ethylene chloride, vinylidene dichloride, trans-dichloroethylene, cis-dichloroethylene, chloroform, dichloro-ethane	Flow measured by helium injection and dilution. Sample is withdrawn using a water aspirator. Hydro-carbon samples are withdrawn using a 10 cc syringe for analysis using a Hewlett Packard Model 700 gas chromatograph. A single 15 foot by 1/8 inch column containing Porepak Q is used for hydrocarbon separation. Analytical methods for other components are unknown.

XVII. Emergency Action Plan (EAP) For Air Pollution Episodes

A. Types of Episodes

The alleviation of air pollution episodes as suggested by the U.S. Environmental Protection Agency is based on a preplanned episode emission reduction scheme. The criteria that set this scheme into motion are:

1. Alert Status - The alert level is that concentration of pollutants at which short-term health effects can be expected to occur.

2. Warning Status - The warning level indicates that air quality is continuing to deteriorate and that additional abatement actions are necessary.

3. Emergency Status - The emergency level is that level at which a substantial endangerment to human health can be expected. These criteria are absolute in the sense that they represent a level of pollution that must not be allowed to occur.

B. Sources of Emissions

As outlined in the foregoing in-depth study of "Ethylene Dichloride Manufacture by the Oxychlorination Process" there are usually four continuous streams emitted with several intermittent emissions occasioned by reactor start-up operations, emergency conditions and, in at least one oxychlorination process, by a catalyst conditioning step.

1. Continuous Streams

(a) Main Process Vent Gas

This stream, which generally vents from a scrubber or an absorber, consists of the gross reactor effluent after quenching and trim cooling for recovery of EDC and represents the primary source of emissions from the oxychlorination process.

The amount of vent gas emissions is dependent on a number of factors; including reactor operating conditions, catalyst activity, and the processing scheme employed, see Section III.

(b) Product Fractionation Vent

This normally represents a small stream which may vary in composition to a considerable degree depending upon the type of fractionation system used. In some cases the stream consists of the combined vent from several fractionators and, in many instances, no product fractionation facilities are provided on-site.

(c) Product Storage Losses

Since the vapor pressure of EDC is low at ambient temperature, the product storage tanks are in most cases vented directly to the atmosphere.

(d) Waste By-Product Disposal

The chlorinated by-products are usually sent to an incinerator. In at least one plant, effluent from the incinerator is cooled and sent to absorbers for recovery of HCl with unrecovered HCl and chlorine formed in the incineration removed in a dilute caustic scrubber before atmospheric venting.

2. Intermittent Air Emissions

(a) Reactor Start-Ups

Usually, during these periods (10-20 minutes duration about twice a month) the main process vent gas to the scrubbers will be enriched with 0.1 to 0.5 tons HCl/ton EDC. This can result in increased HCl emissions to the atmosphere.

(b) Emergency Conditions

In an emergency such as a power failure the scrubber will become ineffective with increased quantities of HCl being vented to the atmosphere.

(c) Catalyst Conditioning Step

This procedure will result in some ethylene emission during reactor start-up operations.

C. Abatement Techniques

As the various levels of the pre-planned episode reduction scheme are declared (Alert, Warning and Emergency) a progressive reduction in the amount of air pollutants emitted must be made. This could ultimately lead to total curtailment of pollutant emissions if the emergency level becomes imminent.

Basically the extent of the required cutback in emissions from ethylene dichloride plants will depend on the relative amount of offending constituents contributed by ethylene dichloride production to the overall emissions which resulted in the pollution episode. Specifically, however, each facility should be considered with respect to the degree in which emissions are normally controlled. This should be a factor when determining the actions required in individual plants during the various episodes.

Ethylene dichloride manufacturing facilities generally consist of a single producing train of equipment with one or more reactors depending on the capacity of the plant. A multiple reactor system provides for added flexibility to accomplish a partial reduction in air pollutant emissions during an air pollution alert. The prime option, however, for a partial reduction in emissions is the capability of turning down plant capacity. Emissions are directly proportional to plant throughput. One hour is required to make an orderly shutdown of a single reactor and a minimum of several hours is required for start-up. However, on those plants that are integrated with a unit to produce vinyl chloride by "cracking" EDC, several hours to several days may be required to shutdown and start-up the overall complex. A turndown to 50-60 percent of EDC

capacity can normally be accomplished in two hours or less with a similar period required to resume normal production.

In either of the foregoing options to accomplish a partial reduction in air pollutants, consideration should be given to those plants that do not contain on-site fractionation facilities for further processing, thus, a significant reduction in the production of EDC would require judicious handling of the downstream equipment.

While operating at reduced plant capacity, scrubbing facilities and the main process vent absorber-stripper system should be maintained at normal operating conditions with design liquid flow rates. The reduction in emissions to this equipment should improve their efficiency thus accomplishing a further reduction of polluting constitutents.

During any air pollution episode, intermittent air emissions should be curtailed to the greatest possible extent. Since reactor start-ups will contribute to increased emissions, resumption of reactor operation should not be undertaken until an "all clear" is announced for the episode. Additionally, since mal-operation of the scrubber and/or absorber-stripper will result in a significant increase in pollutant emissions, increased vigilance in the operation of this equipment should be in force.

1. Declaration of Alert Condition

When an alert condition is declared, the episode emission reduction plan is immediately set into motion. Under this plan in addition to notifying the manufacturer of the alert condition it may be deemed necessary to reduce emissions from ethylene dichloride manufacture somewhat to conform in the overall reduction plan set forth by the Environmental Protection Authorities. This may be accomplished by employing one of the foregoing options. The time required to affect the reduction will depend on the route selected and the amount of reduction in plant capacity required. As previously stated, effort should be made to curtail any emissions that would result from intermittent sources. Usually the alert condition can be expected to continue for 12 hours or more.

2. Declaration of Warning Condition

When the air pollution warning episode is announced, a substantial reduction of air contaminants is desirable even to the point of assuming reasonable economic hardship in the cutback of production and allied operations. This could involve a 50-60 percent decrease in EDC production which would reduce the principal source of emission, represented by the main process vent gas, to a value equivalent to the reduction made in plant capacity. The other sources of emissions represented by the product fractionation vent and product storage losses may decrease to some degree by virtue of the reduction made in the producing equipment.

The reduction in operation of the producing units could temporarily result in some increase in emissions during the "Line out period" at the reduced operation.

TABLE ED-17
FINANCIAL IMPACT OF AIR POLLUTION EPISODES
ON MANUFACTURING COSTS
FOR 700 MM LBS./YEAR ETHYLENE DICHLORIDE MANUFACTURING FACILITY

	Typical Existing Plant		Modified Existing Plant		Most Feasible New Plant	
	No Cutback In Production (Table ED-10)	Assuming 8.5 Days Lost Production	No Cutback In Production (Table ED-11)	Assuming 8.5 Days Lost Production	No Cutback In Production (Table ED-11)	Assuming 8.5 Days Lost Production
DIRECT MANUFACTURING COST, $/YR.						
Raw Materials						
99.9% Ethylene @ 3.25¢/lb.	7,420,000	7,235,000	7,385,000	7,200,000	7,384,000	7,200,000
Anhydrous HCl @ 1.75¢/lb.	8,330,000	8,122,000	8,290,000	8,083,000	8,290,000	8,083,000
Catalyst and Chemicals	280,000	273,000	545,000	531,000	545,000	531,000
Labor	140,000	140,000	161,000	161,000	170,000	170,000
Maintenance	280,000	280,000	317,000	317,000	351,000	351,000
Utilities	420,000	410,000	493,000	481,000	292,000	285,000
	16,870,000	16,460,000	17,191,000	16,773,000	17,033,000	16,620,000
INDIRECT MANUFACTURING COST, $/YR.						
Plant Overhead	140,000	140,000	154,000	154,000	187,000	187,000
FIXED MANUFACTURING COST, $/YR.						
Depreciation, Insurance and Property Tax	770,000	770,000	865,000	865,000	903,000	903,000
TOTAL MANUFACTURING COST, $/YR.	17,780,000	17,370,000	18,210,000	17,792,000	18,123,000	17,710,000
GENERAL EXPENSES, $/YR.						
Administration, Sales, Research & Finance	1,470,000	1,470,000	1,500,000	1,500,000	1,527,000	1,527,000
TOTAL COST, $/YR.	19,250,000	18,840,000	19,710,000	19,292,000	19,650,000	19,237,000
Sales, $/Yr.	21,000,000	20,475,000	21,000,000	20,475,000	21,000,000	20,475,000
Profit Before Taxes	1,750,000	1,635,000	1,290,000	1,183,000	1,350,000	1,238,000
Profit After 52% Tax	840,000	785,000	619,000	568,000	648,000	594,000
Cash Flow	1,460,000	1,405,000	1,322,000	1,271,000	1,382,000	1,328,000
ROI (NPAT X 100/Investment)	13.5%	12.7%	8.8%	8.1%	8.9%	8.1%

3. Emergency Condition

When it appears that an air pollution emergency episode is imminent, all air contaminants except those resulting from storage facilities may have to be eliminated immediately. This may be accomplished by ceasing production and allied operations exclusive of emission control equipment to the extent possible without causing injury to persons or damage to equipment. Complete shutdown of the unit will require approximately three to four hours, if done in an orderly fashion. Otherwise there may be excessive emissions for a short (one hour) period of time. Normally, complete cessation of production should not result in increased emissions since the polluting constituents in the stream to the pollution control equipment will rapidly decrease as the plant ceases operation.

D. Economic Considerations

The economic impact on ethylene dichloride manufacturers of curtailing operations during any of the air pollution episodes depends on the duration and number of episodes in a given period. It is indicated that the duration of air pollution episodes is usually one to seven days with meteorology episode potentials as high as 80 per year.[17] The frequency of air pollution episodes in some areas is indicated as being one to four per year. These data do not differentiate between the episode levels. Normally, since the alert level does not require a cutback in production, it will not influence plant economics. Therefore, in discussing economic considerations resulting from the air pollution abatement plan, it is only necessary to estimate the frequency and number of warning and emergency episodes. For the economic study, it has been assumed that three warning and no emergency episodes occur per year. Each warning episode is assumed to require a 50 percent reduction in air contaminants for a period of five and one half days. This then equates to a complete loss in plant production of about eight and one-half days per year.

The financial impact resulting from this loss in production is shown in Table ED-17. This table contains comparative manufacturing costs for a typical existing 700 MM lbs./year oxychlorination facility without extensive pollution control (Table ED-10), a modified existing plant (Table ED-11) and a most feasible new plant (Table ED-11), all of the same capacity. Economics are shown for each of these plants with and without the financial impact accredited to the air pollution episodes. It should be noted that whereas the assumed cutback in ethylene dichloride production for emission control appears small (2.5 percent on a yearly basis), it reduces net profit from 6.5 to 8.5 percent for the three cases shown.

In most cases, a plant producing ethylene dichloride by oxychlorination is part of an integrated chemical complex and the economic effect of curtailing EDC prdocution can not be completely evaluated without considering the effect on other related operations, such as ethylene and chlorine production. In addition, the pollution contributions from these other plants will also be affected as a result of curtailed production.

E. Summary of Estimated Emissions

In the foregoing, a reduction in air pollutant emissions was suggested for the various air pollution levels that may be encountered. This was predicated on an existing plant that incorporates a minimum of air pollution control equipment. Special consideration should be made in the EAP for Air Pollution Episode Avoidance for plants that incorporate control facilities similar to those proposed for the "most feasible modified existing plant" and "most feasible new plant".

The following presents estimated air emissions for a typical present day system with and without extensive pollution control.

Pollutant	Typical Existing Plant Average Emissions, T/T (A)	Most Feasible Modified Plants Average Emissions T/T (B)	Most Feasible New Plants Average Emissions, T/T (C)
Hydrocarbons			
Ethylene	0.0055		
Other Non-Methane Hydrocarbons	0.0224 (D)	0.0007 (D)	
Paritculates & Aerosols	0.0001	0.0009	
NOx		0.0001	0.0001
CO	0.0064		
	0.0344	0.0017	0.0001

(A) Minimum air pollution control (water scrubber on main process gas stream).

(B) Incorporates thermal incinerator and scrubber on process vent stream plus distillation vent condensers and plume burners.

(C) Incorporates thermal incineration with waste heat boiler, caustic scrubber on process and fractionation vent streams and floating roof product storage tanks.

(D) Includes 0.0006 T/T of EDC lost from product storage tanks.

As noted in the above, total emissions for the most feasible modified plant and the most feasible new plant have been reduced to 5.0 percent and 0.3 percent respectively of that estimated for the existing plant with minimum pollution control. However, it should be noted that some NOx emissions result from the inclusion of the incinerating devices.

The particular type and concentration of pollutants in the atmosphere at the time of the episode would dictate the degree to which reductions would be made on the most feasible modified plant and the most feasible new plant. If NOx is the offending material, then it is conceivalbe that some reduction in production in these plants may be required under "Declaration of Warning Condition". If the offending pollutants are in the form of hydrocarbons or particulates, the degree of cutback on the

most feasible modified plants could be proportionally less severe than on the existing plant with minimum air pollution control. In this instance no cutback would be required on the most feasible new plant.

In addition to the above items, variations in the process and processing scheme in the plants should be considered in setting the production cutback requirement during air pollution episodes. For example oxygen based plants have the potential for low emissions. If normal emissions are low, production cutback may not be necessary.

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APPENDIX I

BASIS OF THE STUDY

I. Industry Survey

The study which led to this document was undertaken to obtain information about selected production processes that are practiced in the Petrochemical Industry. The objective of the study was to provide data for the EPA to use in the fulfillment of their obligations under the Clean Air Amendments of 1970.

The information obtained during the study includes industry descriptions, air emission control problems, sources of air emissions, statistics on quantities and types of emissions and descriptions of emission control devices currently in use. The principal source for these data was an Industry Questionnaire but it was supplemented by plant visits, literature searches, in-house background knowledge and direct support from the Manufacturing Chemists Association.

More than 200 petrochemicals are currently produced in the United States, and many of these by two or more different processes. It was obvious that the most immediate need was to study the largest tonnage, fastest growth processes that produce the most pollution. Consequently, the following 32 chemicals (as produced by a total of 41 different processes) were selected for study:

Acetaldehyde (two processes)
Acetic Acid (three processes)
Acetic Anhydride
Acrylonitrile
Adipic Acid
Adiponitrile (two processes)
Carbon Black
Carbon Disulfide
Cyclohexanone
Ethylene
Ethylene Dichloride (two processes)
Ethylene Oxide (two processes)
Formaldehyde (two processes)
Glycerol
Hydrogen Cyanide
Maleic Anhydride
Nylon 6
Nylon 6,6
"Oxo" Alcohols and Aldehydes
Phenol
Phthalic Anhydride (two processes)
Polyethylene (high density)
Polyethylene (low density)
Polypropylene
Polystyrene
Polyvinyl Chloride
Styrene
Styrene - Butadiene Rubber
Terephthalic Acid (1)
Toluene Di-isocyanate (2)
Vinyl Acetate (two processes)
Vinyl Chloride

(1) Includes dimethyl terephthalate.
(2) Includes methylenediphenyl and polymethylene polyphenyl isocyanates.

The Industry Questionnaire, which was used as the main source of information, was the result of cooperative efforts between the EPA, Air Products and the EPA's Industry Advisory Committee. After receiving approval from the Office of Management and Budget, the questionnaire was sent to selected producers of most of the chemicals listed above. The data obtained from the returned questionnaires formed the basis for what have been named "Survey Reports". These have been separately published in four volumes, numbered EPA-450/3-73-005a, b, c, and d and entitled "Survey Reports on Atmospheric Emissions from the Petrochemical Industry - Volumes I, II, III, and IV.

The purpose of the survey reports was to screen the various petrochemical processes into the "more" and "less - significantly polluting processes". Obviously, significance of pollution is a term which is difficult if not impossible to define because value judgements are involved. Recognizing this difficulty, a quantitative method for Significant Emission Index (SEI) was developed. This procedure is discussed and illustrated in Appendix II of this report. Each survey report includes the calculation of an SEI for the petrochemical that is the subject of the report. These SEI's have been incorporated into the Emission Summary Table that constitutes part of this Appendix (Table I). This table can be used as an aid when establishing priorities in the work required to set standards for emission controls on new stationary sources of air pollution in accordance with the terms of the Clean Air Amendments of 1970.

The completed survey reports constitute a preliminary data bank on each of the processes studied. In addition to the SEI calculation, each report includes a general introductory discussion of the process, a process description (including chemical reactions), a simplified process flow diagram, as well as heat and material balances. More pertinent to the air pollution study, each report lists and discusses the sources of air emissions (including odors and fugitive emissions) and the types of air pollution control equipment employed. In tabular form, each reports summarizes the emission data (amount, composition, temperature, and frequency); the sampling and analytical techniques; stack numbers and dimensions; and emission control device data (types, sizes, capital and operating costs, and efficiencies).

Calculation of efficiency on a pollution control device is not necessarily a simple and straight-forward procedure. Consequently, two rating techniques were developed for each type of device, as follows:

1. For flares, incinerators, and boilers a Completeness of Combustion Rating (CCR) and Significance of Emission Reduction Rating (SERR) were used.

2. For scrubbers and dust removal equipment, a Specific Pollutant Efficiency (SE) and a SERR were used.

The bases for these ratings and example calculations are included in Appendix III of this report.

II. In-Depth Studies

The original performance concept was to select a number of petrochemical processes as "significant polluters", on the basis of data contained in completed questionnaires. These processes were then to be studied "in-depth". However, the overall time schedule was such that the EPA requested an initial selection of three processes on the basis that they would probably turn out to be "significant polluters". The processes selected in this manner were:

1. The Furnace Process for producing Carbon Black.

2. The Sohio Process for producing Acrylonitrile.

3. The Oxychlorination Process for producing 1,2 Dichloroethane (Ethylene Dichloride) from Ethylene.

TABLE I
EMISSIONS SUMMARY

	ESTIMATED (1) CURRENT AIR EMISSIONS, MM LBS./YEAR						
	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5)
Acetaldehyde via Ethylene	1.1	0	0	0	0	1.1	86
via Ethanol	0	0	0	0	27	27	27
Acetic Acid via Methanol	0	0	0.01	0	0	0.01	1
via Butane	40	0	0.04	0	14	54	3,215
via Acetaldehyde	6.1	0	0	0	1.3	7.4	490
Acetic Anhydride via Acetic Acid	3.1	0	0	0	5.5	8.6	253
Acrylonitrile (9)	183	0	5.5	0	196	385	15,000
Adipic Acid	0	0.2	29.6	0	0.14	30	1,190
Adiponitrile via Butadiene	11.2	4.7	50.5	0	0	66.4	3,200
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	156	8.1	6.9	21.6	3,870	4,060	17,544
Carbon Disulfide	0.15	0.3	0.1	4.5	0	5.1	120
Cyclohexanone	70	0	0	0	77.5	148	5,700
Dimethyl Terephthalate (+TPA)	91	1.4	0.1	1.0	53	146.5	7,460
Ethylene	15	0.2	0.2	2.0	0.2	17.6	1,240
Ethylene Dichloride via Oxychlorination	95.1	0.4	0	0	21.8	117.3	7,650
via Direct Chlorination	29	0	0	0	0	29	2,300
Ethylene Oxide	85.8	0	0.3	0.1	0	86.2	6,880
Formaldehyde via Silver Catalyst	23.8	0	0	0	107.2	131	1,955
via Iron Oxide Catalyst	25.7	0	0	0	24.9	50.6	2,070
Glycerol via Epichlorohydrin	16	0	0	0	0	16	1,280
Hydrogen Cyanide Direct Process	0.5	0	0.41	0	0	0.91	56
Isocyanates	1.3	0.8	0	0.02	86	88	231
Maleic Anhydride	34	0	0	0	260	294	2,950
Nylon 6	0	1.5	0	0	0	1.5	90
Nylon 6,6	0	5.5	0	0	0	5.5	330
Oxo Process	5.25	0.01	0.07	0	19.5	24.8	440
Phenol	24.3	0	0	0	0	24.3	1,940
Phthalic Anhydride via O-Xylene	0.1	5.1	0.3	2.6	43.6	51.7	422
via Naphthalene	0	1.9	0	0	45	47	160
High Density Polyethylene	79	2.3	0	0	0	81.3	6,400
Low Density Polyethylene	75	1.4	0	0	0	76.4	6,100
Polypropylene	37.5	0.1	0	0	0	37.6	2,950
Polystyrene	20	0.4	0	1.2	0	21.6	1,650
Polyvinyl Chloride	62	12	0	0	0	74	5,700
Styrene	4.3	0.07	0.14	0	0	4.5	355
Styrene-Butadiene Rubber	9.4	1.6	0	0.9	0	12	870
Vinyl Acetate via Acetylene	5.3	0	0	0	0	5.3	425
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	17.6	0.6	0	0	0	18.2	1,460
Totals	1,227.6	49.1	94.2	33.9	4,852.6	6,225.4 (7)	110,220 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) Emissions based on what is now an obsolete catalyst. See Report No. EPA-450/3-73-006 b for up-to-date information.

TABLE I
EMISSION SUMMARY

	ESTIMATED ADDITIONAL (2) AIR EMISSIONS IN 1980, MM LBS./YEAR						
	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5,6)
Acetaldehyde via Ethylene	1.2	0	0	0	0	1.2	96
via Ethanol	0	0	0	0	0	0	0
Acetic Acid via Methanol	0	0	0.04	0	0	0.04	2
via Butane	0	0	0	0	0	0	0
via Acetaldehyde	12.2	0	0	0	2.5	14.7	980
Acetic Anhydride via Acetic Acid	0.73	0	0	0	1.42	2.15	60
Acrylonitrile (9)	284	0	8.5	0	304	596	23,000
Adipic Acid	0	0.14	19.3	0	0.09	19.5	779
Adiponitrile via Butadiene	10.5	4.4	47.5	0	0	62.4	3,010
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	64	3.3	2.8	8.9	1,590	1,670	7,200
Carbon Disulfide	0.04	0.07	0.03	1.1	0	1.24	30
Cyclohexanone	77.2	0	0	0	85.1	162	6,260
Dimethyl Terephthalate (+TPA)	73.8	1.1	0.07	0.84	42.9	118.7	6,040
Ethylene	14.8	0.2	0.2	61.5	0.2	77	2,430
Ethylene Dichloride via Oxychlorination	110	0.5	0	0	25	136	8,800
via Direct Chlorination	34.2	0	0	0	0	34.2	2,740
Ethylene Oxide	32.8	0	0.15	0.05	0	33	2,650
Formaldehyde via Silver Catalyst	14.8	0	0	0	66.7	81.5	1,250
via Iron Oxide Catalyst	17.6	0	0	0	17.0	34.6	1,445
Glycerol via Epichlorohydrin	8.9	0	0	0	0	8.9	700
Hydrogen Cyanide Direct Process	0	0	0	0	0	0	0
Isocyanates	1.2	0.7	0	0.02	85	87	225
Maleic Anhydride	31	0	0	0	241	272	2,720
Nylon 6	0	3.2	0	0	0	3.2	194
Nylon 6,6	0	5.3	0	0	0	5.3	318
Oxo Process	3.86	0.01	0.05	0	14.3	18.2	325
Phenol	21.3	0	0	0	0	21.3	1,704
Phthalic Anhydride via O-Xylene	0.3	13.2	0.8	6.8	113	134	1,100
via Naphthalene	0	0	0	0	0	0	0
High Density Polyethylene	210	6.2	0	0	0	216	17,200
Low Density Polyethylene	262	5	0	0	0	267	21,300
Polypropylene	152	0.5	0	0	0	152.5	12,190
Polystyrene	20	0.34	0	1.13	0	21.47	1,640
Polyvinyl Chloride	53	10	0	0	0	63	4,840
Styrene	3.1	0.05	0.1	0	0	3.25	225
Styrene-Butadiene Rubber	1.85	0.31	0	0.18	0	2.34	170
Vinyl Acetate via Acetylene	4.5	0	0	0	0	4.5	360
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	26.3	0.9	0	0	0	27.2	2,170
Totals	1,547.2	55.9	79.5	80.5	2,588	4,351.9	134,213 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 40, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) See sheet 1 of 3.

TABLE I
EMISSIONS SUMMARY

	Emissions (2), MM Lbs./Year		Estimated Number of New Plants (1973 - 1980)	Total Estimated Capacity MM Lbs./Year	
	Total by 1980	Total Weighted (5) by 1980		Current	By 1980
Acetaldehyde via Ethylene	2.3	182	6	1,160	2,460
via Ethanol	27	27	0	966	966
Acetic Acid via Methanol	0.05	3	4	400	1,800
via Butane	54	3,215	0	1,020	500
via Acetaldehyde	22	1,470	3	875	2,015
Acetic Anhydride via Acetic Acid	10.8	313	3	1,705	2,100
Acrylonitrile (9)	980	38,000	5	1,165	3,700 (8)
Adipic Acid	50	1,970	7	1,430	2,200
Adiponitrile via Butadiene	128.8	6,210	4	435	845
via Adipic Acid	1.1	60	3	280	550
Carbon Black	5,730	24,740	13	3,000	5,000 (8)
Carbon Disulfide	6.3	150	2	871	1,100
Cyclohexanone	310	11,960	10	1,800	3,600
Dimethyl Terephthalate (+TPA)	265	13,500	8	2,865	5,900
Ethylene	94	3,670	21	22,295	40,000
Ethylene Dichloride via Oxychlorination	253	16,450	8	4,450	8,250 (8)
via Direct Chlorination	63	5,040	10	5,593	11,540
Ethylene Oxide	120	9,530	15	4,191	6,800 (8)
Formaldehyde via Silver Catalyst	212.5	3,205	40	5,914	9,000
via Iron Oxide Catalyst	85	3,515	12	1,729	3,520 (8)
Glycerol via Epichlorohydrin	25	2,000	1	245	380
Hydrogen Cyanide Direct Process	0.5 (10)	28 (10)	0	412	202
Isocyanates	175	456	10	1,088	2,120
Maleic Anhydride	566	5,670	6	359	720
Nylon 6	4.7	284	10	486	1,500
Nylon 6,6	10.8	650	10	1,523	3,000
Oxo Process	43	765	6	1,727	3,000
Phenol	46	3,640	11	2,363	4,200
Phthalic Anhydride via O-Xylene	186	1,522	6	720	1,800 (8)
via Naphthalene	47	160	0	603	528
High Density Polyethylene	297	23,600	31	2,315	8,500
Low Density Polyethylene	343	27,400	41	5,269	21,100
Polypropylene	190	15,140	32	1,160	5,800
Polystyrene	43	3,290	23	3,500	6,700
Polyvinyl Chloride	137	10,540	25	4,375	8,000
Styrene	7.4	610	9	5,953	10,000
Styrene-Butadiene Rubber	14	1,040	4	4,464	5,230
Vinyl Acetate via Acetylene	9.8	785	1	206	356
via Ethylene	TR	TR	4	1,280	2,200
Vinyl Chloride	45	3,630	10	5,400	13,000
Totals	10,605 (7)	244,420 (7)			

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(8) By 1985.
(9) See sheet 1 of 3
(10) Due to anticipated future shut down of marginal plants.

In order to obtain data on these processes, the operators and/or licensors of each were approached directly by Air Products' personnel. This, of course, was a slow and tedious method of data collection because mass mailing techniques could not be used, nor could the request for data be identified as an "Official EPA Requirement". Yet, by the time that OMB approval was given for use of the Industry Questionnaire, a substantial volume of data pertaining to each process had already been received. The value of this procedure is indicated by the fact that first drafts of these three reports had already been submitted to the EPA, and reviewed by the Industry Advisory Committee, prior to the completion of many of the survey reports.

In addition, because of timing requirements, the EPA decided that three additional chemicals be "nominated" for in-depth study. These were phthalic anhydride, formaldehyde and ethylene oxide. Consequently, four additional in-depth studies were undertaken, as follows:

1. Air Oxidation of Ortho-Xylene to produce Phthalic Anhydride.

2. Air Oxidation of Methanol in a Methanol Rich Process to produce Formaldehyde over a Silver Catalyst. (Also, the subject of a survey report.)

3. Air Oxidation of Methanol in a Methanol-Lean Process to produce Formaldehyde over an Iron Oxide Catalyst.

4. Direct Oxidation of Ethylene to produce Ethylene Oxide.

The primary data source for these was the Industry Questionnaire, although SEI rankings had not been completed by the time the choices were made.

The Survey Reports, having now been completed are available, for use in the selection of additional processes for in-depth study.

INTRODUCTION TO APPENDIX II AND III

The following discussions describe techniques that were developed for the single purpose of providing a portion of the guidance required in the selection of processes for in-depth study. It is believed that the underlying concepts of these techniques are sound. However, use of them without substantial further refinement is discouraged because the data base for their specifics is not sufficiently accurate for wide application. The subjects covered in the Appendix II discussion are:

1. Prediction of numbers of new plants.

2. Prediction of emissions from the new plants on a weighted (significance) basis.

The subject covered in the Appendix III discussion is:

Calculation of pollution control device efficiency on a variety of bases, including a weighted (significance) basis.

It should be noted that the weighting factors used are arbitrary. Hence, if any reader of this report wishes to determine the effect of different weighing factors, the calculation technique permits changes in these, at the reader's discretion.

APPENDIX II

Number of New Plants*

Attached Table 1 illustrates the format for this calculation. Briefly, the procedure is as follows:

1. For each petrochemical that is to be evaluated, estimate what amount of today's production capacity is likely to be on-stream in 1980. This will be done by subtracting plants having marginal economics due either to their size or to the employment of an out-of-date process.

2. Estimate the 1980 demand for the chemical and assume a 1980 installed capacity that will be required in order to satisfy this demand.

3. Estimate the portion of the excess of the 1980 required capacity over today's remaining capacity that will be made up by installation of each process that is being evaluated.

4. Estimate an economic plant or unit size on the basis of today's technology.

5. Divide the total required new capacity for each process by the economic plant size to obtain the number of new units.

In order to illustrate the procedure, data have been incorporated into Table I, for the three processes for producing carbon black, namely the furnace process, the relatively non-polluting thermal process, and the non-growth channel process.

*The format is based on 1980, but any future year may be selected.

Table 1. Number of New Plants by 1980

Chemical	Process	Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
Carbon Black	Furnace	4,000	0	4,000	4,500	5,000	1,000	90	11 - 12
	Channel	100	0	100	100	100	0	30	0
	Thermal	200	0	200	400	500	300	150	2

Notes: 1. Capacity units all in MM lbs./year.

2. 1980 demand based on studies prepared for EPA by Processes Research, Inc. and MSA Research Corporation.

Increased Emissions (Weighted) by 1980

Attached Table 2 illustrates the format for this calculation. However, more important than format is a proposal for a weighting basis. There is a wide divergence of opinion on which pollutants are more noxious and even when agreement can be reached on an order of noxiousness, disagreements remain as to relative magnitudes for tolerance factors. In general pollutants from the petrochemical industry can be broken down into categories of hydrogen sulfide, hydrocarbons, particulates, carbon monoxide, and oxides of sulfur and nitrogen. Of course, two of these can be further broken down; hydrocarbons into paraffins, olefins, chlorinated hydrocarbons, nitrogen or sulfur bearing hydrocarbons, etc. and particulates into ash, catalyst, finely divided end products, etc. It was felt that no useful end is served by creating a large number of sub-groupings because it would merely compound the problem of assigning a weighting factor. Therefore, it was proposed to classify all pollutants into one of five of the six categories with hydrogen sulfide included with hydrocarbons.

There appears to be general agreement among the experts that carbon monoxide is the least noxious of the five and that NO_x is somewhat more noxious than SO_x. However, there are widely divergent opinions concerning hydrocarbons and particulates - probably due to the fact that these are both widely divergent categories. In recent years, at least two authors have attempted to assign tolerance factors to these five categories. Babcock (1), based his on the proposed 1969 California standards for one hour ambient air conditions with his own standard used for hydrocarbons.

On the other hand, Walther (2), based his ranking on both primary and secondary standards for a 24-hour period. Both authors found it necessary to extrapolate some of the basic standards to the chosen time period. Their rankings, on an effect factor basis with carbon monoxide arbitrarily used as a reference are as follows:

	Babcock	Walther	
		Primary	Secondary
Hydrocarbons	2.1	125	125
Particulates	107	21.5	37.3
NO_x	77.9	22.4	22.4
SO_x	28.1	15.3	21.5
CO	1	1	1

Recognizing that it is completely unscientific and potentially subject to substantial criticism it was proposed to take arithmetic averages of the above values and round them to the nearest multiple of ten to establish a rating basis as follows:

	Average	Rounded
Hydrocarbons	84.0	80
Particulates	55.3	60
NO_x	40.9	40
SO_x	21.6	20
CO	1	1

Table 2. Weighted Emission Rates

Chemical _____

Process _____

Increased Capacity _____

Pollutant	Emissions, Lbs./Lb.	Increased Emissions Lbs./Year	Weighting Factors	Weighted Emissions Lbs./Year
Hydrocarbons			80	
Particulates			60	
NO_x			40	
SO_x			20	
CO			1	
			Total	

Increased Emissions (Weighted) by 1980 (continued)

This ranking can be defended qualitatively, if not quantitatively for the following reasons:

1. The level of noxiousness follows the same sequence as is obtained using national air quality standards.

2. Approximately two orders of magnitude exist between top and bottom rankings.

3. Hydrocarbons should probably have a lower value than in the Walther analysis because such relatively non-noxious compounds as ethane and propane are included.

4. Hydrocarbons should probably have a higher value than in the Babcock analysis because such noxious (or posionous) substances as aromatics, chlorinated hydrocarbons, phenol, formaldehyde, and cyanides are included.

5. Particulates should probably have a higher value than in the Walther analysis because national air standards are based mostly on fly ash while emissions from the petrochemical industry are more noxious being such things as carbon black, phthalic anhydride, PVC dust, active catalysts, etc.

6. NO_x should probably have a higher value than in the Walther analysis because its role in oxidant synthesis has been neglected. This is demonstrated in Babcock's analysis.

Briefly, the procedure, using the recommended factors and Table 2, is as follows:

1. Determine the emission rate for each major pollutant category in terms of pounds of pollutant per pound of final product. (This determination was made, on the basis of data reported on returned questionnaires, in the Survey Reports).

2. Multiply these emission rates by the estimate of increased production capacity to be installed by 1980 (as calculated while determining the number of new plants), to determine the estimated pounds of new emissions of each pollutant.

3. Multiply the pounds of new emissions of each pollutant by its weighting factor to determine a weighted pounds of new emissions for each pollutant.

4. Total the weighted pounds of new emissions for all pollutants to obtain an estimate of the significance of emission from the process being evaluated. It was proposed that this total be named "Significant Emission Index" and abbreviated "SEI".

It should be pointed out that the concepts outlined above are not completely original and considerable credit should be given to Mr. L. B. Evans of the EPA for setting up the formats of these evaluating procedures.

Increased Emissions (Weighted) by 1980 (continued)

(1) Babcock, L. F., "A Combined Pollution Index for Measurement of Total Air Pollution," JAPCA, October, 1970; Vol. 20, No. 10; pp 653-659

(2) Walther, E. G., "A Rating of the Major Air Pollutants and Their Sources by Effect", JAPCA, May, 1972; Vol. 22, No. 5; pp 352-355

Appendix III
Efficiency of Pollution Control Devices

Incinerators and Flares

The burning process is unique among the various techniques for reducing air pollution in that it does not remove the noxious substance but changes it to a different and hopefully less noxious form. It can be, and usually is, a very efficient process when applied to hydrocarbons, because when burned completely the only products of combustion are carbon dioxide and water. However, if the combustion is incomplete a wide range of additional products such as cracked hydrocarbons, soot and carbon monoxide might be formed. The problem is further complicated if the hydrocarbon that is being burned is halogenated, contains sulfur or is mixed with hydrogen sulfide, because hydrogen chloride and/or sulfur oxides then become products of combustion. In addition, if nitrogen is present, either as air or nitrogenated hydrocarbons, oxides of nitrogen might be formed, depending upon flame temperature and residence time.

Consequently, the definition of efficiency of a burner, as a pollution control device, is difficult. The usual definition of percentage removal of the noxious substance in the feed to the device is inappropriate, because with this definition, a "smoky" flare would achieve the same nearly 100 percent rating, as a "smokeless" one because most of the feed hydrocarbon will have either cracked or burned in the flame. On the other hand, any system that rates efficiency by considering only the total quantity of pollutant in both the feed to and the effluent from the device would be meaningless. For example, the complete combustion of one pound of hydrogen sulfide results in the production of nearly two pounds of sulfur dioxide, or the incomplete combustion of one pound of ethane could result in the production of nearly two pounds of carbon monoxide.

For these reasons, it was proposed that two separate efficiency rating be applied to incineration devices. The first of these is a "Completeness of Combustion Rating" and the other is a "Significance of Emission Reduction Rating", as follows:

1. Completeness of Combustion Rating (CCR)

This rating is based on oxygen rather than on pollutants and is the pounds of oxygen that react with the pollutants in the feed to the device, divided by the theoretical maximum number of pounds that would react: Thus a smokeless flare would receive a 100 percent rating while a smoky one would be rated somewhat less, depending upon how incomplete the combustion.

In utilizing this rating, it is clear that carbon dioxide and water are the products of complete combustion of hydrocarbons. However, some question could occur as to the theoretical completion of combustion when burning materials other than hydrocarbons. It was recommended that the formation of HX be considered complete combustion of halogenated hydrocarbons since the oxidation most typically does not change the valence of the halogen. On the other hand, since some incinerators will be catalytic in nature it was recommended that sulfur trioxide be considered as complete oxidation of sulfur bearing compounds.

Efficiency of Pollution Control Devices

1. Completeness of Combustion Rating (CCR) (continued)

Nitrogen is more complex, because of the equilibria that exist between oxygen, nitrogen, nitric oxide, nitrogen dioxide and the various nitrogen radicals such as nitrile. In fact, many scientists continue to dispute the role of fuel nitrogen versus ambient nitrogen in the production of NO_x. In order to make the CCR a meaningful rating for the incineration of nitrogenous wastes it was recommended that complete combustion be defined as the production of N_2, thus assuming that all NO_x formed comes from the air rather than the fuel, and that no oxygen is consumed by the nitrogen in the waste material. Hence, the CCR becomes a measure of how completely the hydrocarbon content is burned, while any NO_x produced (regardless of its source) will be rated by the SERR as described below.

2. Significance of Emission Reduction Rating (SERR)

This rating is based primarily on the weighting factors that were proposed above. All air pollutants in the feed to the device and all in the effluents from the device are multiplied by the appropriate factor. The total weighted pollutants in and out are then used in the conventional manner of calculating efficiency of pollutant removal, that is pollutants in minus pollutants out, divided by pollutants in, gives the efficiency of removal on a significance of emission basis.

Several examples will serve to illustrate these rating factors. as follows:

Example 1 - One hundred pounds of ethylene per unit time is burned in a flare, in accordance with the following reaction:

$$3C_2H_4 + 7\,O_2 \longrightarrow C + 2\,CO + 3\,CO_2 + 6\,H_2O$$

Thus, 14.2 lbs. of particulate carbon and 66.5 lbs. of carbon monoxide are emitted, and 265 lbs. of oxygen are consumed.

Theoretical complete combustion would consume 342 lbs. of oxygen in accordance with the following reaction:

$$C_2H_4 + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O$$

Thus, this device would have a CCR of 265/342 or 77.5%

Assuming that one pound of nitric oxide is formed in the reaction as a result of the air used for combustion (this is about equivalent to 100 ppm), a SERR can also be calculated. It should be noted that the formation of this NO is not considered in calculating a CCR because it came from nitrogen in the air rather than nitrogen in the pollutant being incinerated. The calculation follows:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

Pollutant	Weighting Factor	Pounds in		Pounds out	
		Actual	Weighted	Actual	Weighted
Hydrocarbons	80	100	8000	0	
Particulates	60	0		14.2	852
NO_x	40	0		1	40
SO_x	20	0		0	
CO	1	0		66.5	66.5
Total			8000		958.5

$$SERR = \frac{8000 - 958.5}{8000} \times 100 = 88\%$$

Example 2 - The same as Example 1, except the hydrocarbons are burned to completion. Then,

$$CCR = \frac{342}{342} \times 100 = 100\%$$

and

$$SERR = \frac{8000 - 40}{8000} = 99.5\%$$

Example 3 - One hundred pounds per unit time of methyl chloride is incinerated, in accordance with the following reaction.

$$2\ CH_3Cl + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O + 2\ HCl$$

This is complete combustion, by definition, therefore, the CCR is 100%. However, (assuming no oxides of nitrogen are formed), the SERR is less than 100% because 72.5 lbs. of HCl are formed. Hence, considering HCl as an aerosol or particulate;

$$SERR = \frac{100 \times 80 - 72.5 \times 60}{100 \times 80} \times 100 = 45.5\%$$

The conclusion from this final example, of course, is that it is an excellent combustion device but a very poor pollution control device, unless it is followed by an efficient scrubber for HCl removal.

Example 4 - The stacks of two hydrogen cyanide incinerators, each burning 100 pounds per unit time of HCN are sampled. Neither has any carbon monoxide or particulate in the effluent. However, the first is producing one pound of NO_x and the second is producing ten pounds of NO_x in the same unit time. The assumed reactions are:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

$$4\ HCN + 5\ O_2 \longrightarrow 2\ H_2O + 4\ CO_2 + 2\ N_2$$

$$N_2\ (\text{atmospheric}) + XO_2 \longrightarrow 2\ NO_x$$

Thus, $CCR_1 = 100\%$ and $CCR_2 = 100\%$ both by definition.

However, $SERR_1 = \frac{100 \times 80 - 1 \times 40}{100 \times 80} \times 100 = 99.5\%$

and $SERR_2 = \frac{100 \times 80 - 10 \times 40}{100 \times 80} \times 100 = 95\%$

Obviously, if either of these were "smoky" then both the CCR and the SERR would be lower, as in Example 1.

Other Pollution Control Devices

Most pollution control devices, such as bag filters, electrostatic precipitators and scrubbers are designed to physically remove one or more noxious substances from the stream being vented. Typically, the efficiency of these devices is rated relative only to the substance which they are designed to remove and for this reason could be misleading. For example:

1. The electrostatic precipitator on a power house stack might be 99% efficient relative to particulates, but will remove little or none of the SO_x and NO_x which are usually present.

2. A bag filter on a carbon black plant will remove 99 + % of the particulate but will remove none of the CO and only relatively small amounts of the compounds of sulfur that are present.

3. A water scrubber on a vinyl chloride monomer plant will remove all of the hydrogen chloride but only relatively small amounts of the chlorinated hydrocarbons present.

4. An organic liquid scrubber on an ethylene dichloride plant will remove nearly all of the EDC but will introduce another pollutant into the air due to its own vapor pressure.

For these reasons, it was suggested again that two efficiency ratings be applied. However, in this case, the first is merely a specific efficiency as is typically reported, i.e., "specific to the pollutant (or pollutants) for which it was designed", thus:

$$SE = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

The second rating proposed is an SERR, defined exactly as in the case of incinerators.

Two examples will illustrate these ratings.

Efficiency of Pollution Control Devices

Other Pollution Control Devices (continued)

Example 1 - Assume that a catalytic cracker regenerator effluent contains 100 pounds of catalyst dust, 200 lbs. of carbon monoxide and 10 pounds of sulfur oxides per unit time. It is passed through a cyclone separator where 95 pounds of catalyst are removed. Therefore,

$$SE = \frac{100 - 5}{100} \times 100 = 95\%$$

$$\text{and } SERR = \frac{(100 \times 60 + 10 \times 20 + 200 \times 1) - (5 \times 60 + 10 \times 20 + 200 \times 1)}{(100 \times 60 + 10 \times 20 + 200 \times 1)} \times 100$$

$$= \frac{6400 - 700}{6400} \times 100 = 89\%$$

Example 2 - Assume that an organic liquid scrubber is used to wash a stream containing 50 pounds of SO_2 per unit time. All but one pound of the SO_2 is removed but two pounds of the hydrocarbon evaporate into the vented stream. Then

$$SE = \frac{50 - 1}{50} \times 100 = 98\%$$

$$\text{and } SERR = \frac{(50 \times 20) - (1 \times 20 + 2 \times 80)}{(50 \times 20)} \times 100$$

$$= \frac{1000 - 180}{1000} \times 100 = 82\%$$